

**Water Quality Concerns
and
Treatment Parameters for Armanda Lake**

by

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March 1, 2001

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Water Quality Concerns and Treatment Parameters for Armanda Lake

1.0 Introduction

Mud Lake receives contaminated groundwater flow originating from the tailings deposit at the abandoned South Bay mine site in Northern Ontario. Mud Lake surface water outflow discharges to the outlet end of Armanda Lake, which then discharges to Confederation Lake at long term monitoring station C11 (see Map1, given at the end of the report). Recent sampling in Armanda Lake has demonstrated unforeseen pH depression in this Lake. This report briefly summarizes historic remedial activity in Mud Lake, describes the recently observed pH depression in Armanda Lake, and recommends a course of action for reversing the pH depression and enhancing the buffering capacity of Armanda Lake sediments through the application of locally available waste wood ash. We feel that treatment is required as soon as possible to prevent further pH decline in Armanda Lake, while we institute longer term controls (i.e. contaminated groundwater treatment) “upstream” in the so-called “Kalin Canyon” and Mud Lake.

2.0 Recent Background

2.1 Review of Remedial Actions in Mud Lake

In 1994 the ground water discharge from the tailings emerged in Mud Lake. The discharge was quantified, using both the surface water flow estimates and chemical data to arrive at discharge volumes of 1 L/s. With this discharge, it was estimated that 46 t of iron and 3.5 t of zinc were discharged to Mud Lake annually. Measures to retain the contaminants were underway in May 1995, with the installation of an ARUM cover in the Lake in the area of ground water discharge.

Unfortunately, the installation failed, due to the heavy encrustment /precipitation of iron on the floating cover, which could not stay afloat (Plate 2). The desired reducing conditions in the sediment (enhanced with potato waste addition to sediment) could not be established. The reducing conditions would have lead to pH increase and concurrent contaminant reduction (Kalin et. al 1999). This approach had to be abandoned by the end of 1996.

Instead, 60 t of natural phosphate rock were added to the sediment to precipitate oxidized iron phosphate in June 1997 (Plate1). Iron phosphate precipitate is stable at low pH (Garrels & Christ 1966 and Baron & Palmer 1996). The effects of the phosphate rock application are shown in **Figure 1**. The iron concentrations dropped immediately from 196 to 48.7 mg/l in Mud Lake.

Zinc and iron concentrations in the water column are somewhat linked. The concentration of zinc is 5 times lower than iron in Mud Lake Outflow and Mud Lake Middle (**Figure 2**). If iron is precipitated from the water, then through adsorption and co-precipitation processes also some zinc is removed from the water column, both from the natural iron-hydroxide precipitation and the enhanced precipitation with phosphate. Phosphate rock also contains carbonate, which adds to the neutralizing capacity of the sediments.

Precipitate particles were collected in Mud Lake in sedimentation traps from 1994 to 1998. Before phosphate application the iron content in the precipitate ranged from 20% to 42% and from 0.03% to 0.17% for zinc. Within Mud Lake the sedimentation rate is about 14 g/m². After phosphate application the iron hydroxide precipitate contained 43% iron and 0.43% zinc. The estimates indicated that 37 t of iron and 0.37 t of zinc per year are converted to solids settling to the sediments. These estimates are derived from sedimentation rates and elemental analysis of the collected precipitate. They are within the range of annual loading of contaminants from the ground water to Mud Lake (i.e. 46 t of iron and 3.5 t of zinc) confirming that a large fraction of the contaminants are retained within Mud Lake.

This first cut estimate of contaminant retention in the sediments represents a very rough assessment. Mass balances of elemental cycling and retention of lakes are considerably more complex. A more detailed assessment, considering iron cycling dynamics for the Mud Lake system (sediment, pore-water, and ground water input and surface water out flow) is in preparation.

Particularly complex is iron cycling in AMD lakes as iron oxidation and reduction reactions are controlling pH, which in turn affects iron and other metals solubility. In addition in AMD lakes strong concentration gradients are present between sediment and water inter-phase, which affect final concentrations in the water. Of outmost importance for iron cycling is pH control, as it's hydroxide forms only at pH higher then 2.0.

The remedial action of adding phosphate application has a three-fold effect. First it reduces the iron concentration which reduces the amount of iron available for cycling from the sediment to the water through bio-geochemical oxidation. Iron phosphate precipitate is more stable than iron hydroxide. Second, with less iron available to be recycled from the sediment, the pH depression in the summer should be lower. Third the natural phosphate rock contains some carbonate which should add buffer capacity to the sediment.

It was therefore expected that the phosphate application to Mud Lake should have lead to a reduction of the summer pH depressions in Mud Lake would occur. This reduction is depicted in Figure 3a and 3b for the sampling location in the center of Mud Lake and in Mud Lake outflow. The pH in 1996 was once as low as 2.2 and increased after the phosphate application to 3.6 in the beginning dropping to 2.8 by the end of 1997 and has remained around this value up to 2000. As mentioned earlier, a pH value of around pH 2.0 would result in less iron precipitate, an undesirable state. This has not occurred in Mud Lake and also not in the water leaving at the Outflow. With the pending scale up of contaminated groundwater treatment in 2001, an overall improvement in Mud Lake conditions is anticipated.

Overall, the beneficial effect of phosphate rock additions is substantiated based on the 1997-2000 results. These improvements were required, as time for development of the in situ groundwater treatment research program was needed. This program was initiated in 1997 and was completed by the end of 2000. A separate report will be submitted to the Ministry of Environment, in support of groundwater treatment scale-up. The NRC report has been submitted and a second experimental series of testing the microbial alkalinity generation is in progress during winter 2000/2001.

2.2 Mud Lake Discharge Effects on Armanda Lake

Owing to the linkage between Mud and Armanda Lakes, and the general proximity of Lena Lake ([Map 1](#)), periodic water quality monitoring was initiated in Armanda and Lena Lakes in early 1995. These data are presented in [Table 1a and 1b](#), and are discussed in more details later. Sampling locations are shown in [Map 2](#). The water samples are mostly obtained during the winter months, because only then is access possible relatively easily by snowmobile. Since 1995 Lena Lake was regularly sampled, due to our concern of contaminated ground water escaping to Lena Lake. Lena Lake has remained in good conditions since 1995. None of the measured parameters have changed.

Armanda Lake was added to the sampling irregularly, as we had constructed a predictive model for the known effluent from Mud Lake, and intended to confirm or reject our model predictions. The spreadsheet model estimating the effects of Mud Lake outflow on Armanda Lake was constructed in 1996/1997, as we had reasonable estimates of the volumes of water leaving Mud Lake.

The spreadsheet model used the drainage basin run-off to estimate the flows from Mud Lake to Armanda Lake, and the flows, which are received from Lena Lake in order to predict the water quality changes in Armanda Lake. The dimensions used to arrive at the run-off quantities are given in [Table 2](#). The drainage basin boundaries are shown in [Map 1](#). The estimates are compared to flow measurements taken at the outflow of Mud

Lake and they agree reasonably well (Table 2).

This model, when run using steady flow leaving Mud Lake and annual average concentrations leaving Mud Lake, suggested that zinc concentrations in Armanda Lake should be higher than were measured (Figure 4). The difference was attributed to precipitation and adsorption of zinc taking place in the muskeg between Mud Lake and Armanda Lake (Plate 3). Although the predictions with steady flow and seasonal average concentrations instead of annual averages as inputs to the model achieved a better fit between modeled and measured zinc concentrations, Armanda Lake appeared to be in no serious jeopardy from a contaminants perspective, particularly given that:

- 1) planning was in progress for treatment of contaminated groundwater inputs to Mud Lake (i.e. groundwater treatment scale-up).
- 2) Further polishing capacity exists both in Armanda Lake and in the muskeg between Armanda Lake and Confederation Lake at long term monitoring station C11 (Map 2).
- 3) Polishing between Mud Lake and Armanda Lake appeared to be also adding to the contaminant reduction.

We concentrated instead on the in situ groundwater treatment and the scale up possibilities. Most importantly in the context of Armanda Lake, this included a conscious decision to allow beaver activity at the outflow of Mud Lake, which had started by mid 1998, to dam up the outflow of Mud Lake. An increased the water level in Mud Lake provided us with an opportunity to monitor groundwater response in the drainage basin containing the tailings deposit, essentially a perfect opportunity to validate our groundwater model for the area. The model, constructed with Visual Modflow, was developed by Waterloo Hydro-geologic and is used to support the in-situ groundwater treatment research.

The measured groundwater response to 0.6 m rise in Mud Lake water level confirmed the accuracy and validity of our groundwater model for the entire drainage basin. The

most important finding from utilizing the beaver dam to verify our model was that the proposed in situ treatment scale up will address all groundwater contaminants from the tailings. No other groundwater path exists from the tailings area to Confederation Lake, Armanda Lake or to Lena Lake. All contaminated groundwater is discharging to Mud Lake and to Armanda Lake as surface water.

In the longer term, increasing the water level of Mud Lake by about 0.6 m is highly undesirable, as it increases the tailings mass which is exposed to water level fluctuations. Therefore, on completion of the groundwater model evaluation we breached the beaver dam on the outflow from Mud Lake. Permission was obtained in June 2000 from MNR to breach the beaver dam, and install a beaver 'unfriendly' pipe in the lowered beaver dam, to maintain low, normal Mud Lake water levels.

We did consider and account for the potential effects relating to metals loading. Due to the hydraulic head difference, we were discharging less iron and zinc into Mud Lake during the high water level period. In Figure 5a and 5b the seasonal zinc concentrations are given for the years 1996 to 2000 for Mud lake center and Mud lake outflow. The years 1999 and 2000 showed the lowest concentrations compared to the previous years, remaining in both years below 15 mg/l throughout the year for Mud lake center and below 10 mg/l for the outflow. This compares to the previous years where the concentrations were above 15 mg/L in the center or as high as 25 mg/L. We expected that the reduction in discharge would more or less balance the effects of the sudden metal loading to Armanda Lake following breach of the beaver dam in the long run. So, while we did address net metal loading to Armanda Lake, we did not address the effect on pH. The sudden release of low pH water over a short period of time we did not account for and hence the impact pH in Armanda Lake. The net effect has been a recent abrupt pH depression in Armanda Lake, evident in Table 1b.

This abrupt depression was first noticed in samples collected December 31, 2000. Upon receipt of the data from the lab, we promptly re-sampled, on February 1, 2001, in order to verify the current situation.

3.0 Variability in pH Monitoring Data, Lab vs Field Measurement

Although the pH measurement is carefully obtained, by buffering the probe with buffer solutions prior to reading in the appropriate pH span, solutions around pH 7 are very difficult to read. The probe is sensitive only to active hydrogen ions, which are affected around this value by natural buffer systems (carbonate and silicate). A brief discussion is therefore provided which demonstrates the range of values, which can be obtained under field and laboratory conditions.

To obtain a pH measurement around the near-neutral pH value in highly dilute water is notoriously difficult, if the same reading is to be obtained with any consistency. Therefore differences between field and laboratory values are often found. Data on pH differences for Armanda, Lena, and Confederation Lakes (C11) are summarized in [Figure 6a and 6b](#). For other stations in Confederation Lake the data are given for Boomerang lake outflow in Lost Bay (C1) and the surface and bottom measurements for station C8, located in mine site bay in Confederation Lake. Although the same pH probes are used for both field and laboratory measurements, the differences can be substantial; typically, lower values are associated with measurement in the lab. This is the case for all stations which are in the difficult pH range around 6 to 7. Of course, the outflow from Boomerang Lake (C1) reports the largest range due to some winter discharges of low pH water from Boomerang Lake. The pH value differences are attributable to biological activity in the water, degassing, temperature and in addition, and the more common measurement variability associated with sampling and operators of the instruments.

In [Table 3](#) the pH of the most recent water samples are presented for Armanda Lake. The pH values were determined on the sample collected in December 31st. They traveled in coolers to the Toronto Laboratory arriving on January the 4th. These pH values triggered the alertness and we re-sampled on February 1st. Those samples were re-measured over a two weeks period, showing smaller differences in pH for the same stations. Although the water was collected through more or less the same hole drilled

through the ice, and at depth below the ice, the pH values differ somewhat. The main point of this discussion is to draw the attention to the fact, that the pH value of 5.7, which was reported in 1997 for Armanda Lake, could not have had the same warning impact, as the present conditions (Table 3).

Arguably, the pH value of 5.77 measured in the field in 1997 at station ML44 should perhaps have raised concern, alerting us earlier to the progressive pH decline in Armanda Lake (Table 1a). Given the known variations in pH, lower values alone are not indicative of problems. As the other parameters monitored (Acidity, sulphate, Zn and Fe) were within the normal range of Armanda Lake. Therefore this pH value did not raise any particular concern.

4.0 Modeling pH Decline in Armanda Lake

In hindsight, in addition to modeling the metal load from Mud Lake to Armanda Lake, we should also have modeled pH effects. In order to capitalize on any attendant insights, this work was initiated immediately after the low pH values were reported in December 2000. This work is summarized following.

In **Table 4** the arithmetic method of calculating the pH following mixing of two solutions of different pH and volume is shown. It uses a quadratic equation to solve for the number of excess moles of H^+ and OH^- which react to form H_2O . The concentration of H^+ remaining determines the mixed solution's pH.

A quadratic equation takes the volume (in m^3) of water leaving Mud Lake (ML18) at a given average pH over a month and mixes this volume completely with the volume of Armanda Lake ($1,000,000 m^3$) with an initial measured pH. Solving the equation leads to a new pH for this month. This new estimated pH of Armanda Lake ($1,000,000 m^3$) is then mixed in the next step with the volume of clean run-off entering the Armanda Lake for that month with a neutral pH to yield the final pH for Armanda Lake for these months. This final pH is used as the initial pH for calculation of the next month's pH estimate,

repeating the process for each month.

In [Figure 7](#) the conditions with the beaver dam intact are modeled in the way described above. For the last years conditions taking the original pH of Armanda lake as 5.4 with the discharge from Mud lake, we would have expected a pH of 3.5 in Armanda lake. Measured Armanda Lake pHs for December, 2000 and early February, 2001 are shown. The measured values of pH are higher than would be expected from the model when input pH of 2.7 is used.

The situation when the beaver dam is breached is illustrated in [Figure 8](#), producing the expected pH of Armanda Lake for the months following breaching of the beaver dam. In June, 2000 the beaver dam at Mud Lake outflow was breached, lowering the water level 0.6 m over 13 days. This released a large volume ($126,600 \text{ m}^3$) of low pH water (3.5 used in calculation) to Armanda Lake (pH 5.41 measured in March 2000). These estimates also used an initial Armanda Lake pH of 5.41 (March 2000), and pH 2.7 as the Mud Lake outflow value. The difference to the un-breached beaver dam is that the pH depression would have been lower (3.3) than with the regular discharge (between the modeled and measured pH are attributable 3.6) both at the same time, ie more or less immediately.

Two assumptions used in this modeling approach will contribute to a delay in time when the pH depression is occurring. Firstly the assumption of instantaneous mixing of the two waters is unrealistic and second, the flow conditions which are assumed as average throughout the year do not take place as noted from the measured min and max at Mud lake outflow (Table 2).

In addition to these factors, a further key unknown entity which creates discrepancy between the measured and modeled results is the buffering capacity of the lake sediments (Anderson and Schiff 1987 and Dam and Buskens 1993). In both modeled cases regular discharge and beaver dam breached ([Figures 7](#) and [Figures 8](#)) the measured values are higher than those expected from the model

To demonstrate buffering capacity of the lake and its sediments, in [Figure 9](#) we model the long term situation 1) slow acidification and 2) in [Figure 10](#) rapid acidification simulating the beaver-dam break, using the same approach as outlined in Table 4. Again for the model, both scenarios (slow and rapid acidification) we used measured average value of pH as input from Mud Lake to Armanda Lake for 1995 and 1996. The initial pH depression differs in the two scenarios. Looking at the long term simulation starting in 1995, even using Mud Lake outflow water with a pH of 2.7(which was not the case throughout this period) the pH should have rapidly decreased. In the slow acidification it would have reached the present pH of 4.5 by 1995 ([Figure 9](#)) and in the rapid acidification the pH would have reached 3.2 by 1995. However, in reality, pH decreases to less than 5.0 did not occur until the year 2000, six years after acidification of Mud Lake was first measured and the discharge to Armanda Lake started.

5.0 pH Model Implications for Treatment Strategy

We can conclude from the preceding model runs (and earlier water chemistry data) that natural sediment buffering capacity has limited the severity of the current pH depression in Armanda Lake. We might further conclude that, in the process, substantial sediment buffering capacity has already been consumed in Armanda Lake. In order to reverse the current pH depression in Armanda Lake, and to build additional capacity to neutralize acidity from Mud Lake, it makes sense to focus on a treatment strategy that augments Armanda Lake sediment buffering capacity while simultaneously contributing alkalinity directly to the water column, treating the water *per se*.

Locally available waste wood ash meets these two treatment criteria. We believe this material would be appropriate and effective as an amendment for the treatment of Armanda Lake. We feel that treatment is required as soon as possible to prevent further pH decline in Armanda Lake, while we institute the longer term controls (i.e. groundwater treatment) “upstream” in the so-called “Kalin Canyon” and Mud Lake. The urgency arises due to the access to Armanda Lake, which is only possible in the winter

time.

6. 0 Treatment of pH Depression in Armanda Lake

6.1 Broad Options and Preferred Approach:

The basic technical case for waste wood ash as a suitable amendment at the South Bay site is presented in a separate and appended report by Boojum Research. In terms of loading rates and delivery mechanisms specific to Armanda Lake, we have explored two different approaches: 1) one-time batch application of bulk wood ash through holes in the Lake ice, this winter; and 2) periodic application of wood ash slurry to Mud Lake outflow, post-breakup. Details are discussed later in this report.

We also reviewed the relative merits of using conventional neutralizing agents i.e. NaOH or $\text{Ca}(\text{OH})_2$ but discounted these alternatives, in favor of wood ash, for a number of specific reasons including:

- Treatment chemicals address the water column but do not augment sediment buffering/neutralizing capacity. Wood ash addresses both.
- Treatment chemicals (particularly caustic) are highly reactive in their bulk state, presenting wildlife safety concerns. Bulk wood ash is relatively inert.
- Infrastructure requirements. Mobile lime treatment would require a power generator at Mud Lake outflow.
- Simplicity. Bulk wood ash through the ice is as simple as it gets.
- Vandalism and theft. Anything sitting in place at site is a target. Wood ash through the ice eliminates this exposure.
- Relative cost.
- Finally, wood ash has the unique benefit of demonstrating a beneficial application for a local waste stream that is currently land filled.

On the strength of the above arguments, we then proceeded with investigations and experimentation to estimate the effective neutralizing capacity of wood ash and

determine the specific volume of wood ash required treating Armanda Lake and reversing the current pH depression.

6.2 Potential Risk of Metal Contamination from Woodash

The selection of an environmental remediation action has to consider the consequences of this action. For conventional treatment chemicals, such as lime or caustic, the consequences are well documented with increases in calcium-sulphate for lime and sodium for caustic. Sludge production is a problem with both of them. Although these consequences would be undesirable for Armanda Lake, a very dilute oligotrophic water, the alternative neutralizing agent, wood-ash raises concerns with respect to metals. Sludge production is not an issue with woodash, as it releases mainly hydroxyl ions with potassium, as compound not as relevant to cell membrane transport as sodium. Sludge production is not an issue, as the alkalinity is mainly released from the sediment. However, the concern would lay with the liberation metals.

This issue is addressed with the analyses of the supernatant solutions from a series of experiments where neutralizing capacity was quantified. If we add wood-ash to a lake, we have to account for release of metals in several scenarios. Wood-ash will sink to the sediment where a high density or ratio of wood-ash and water can be envisaged. These conditions are simulated with high solid :liquid ratio (1:5). A second scenario examines the solubility of wood-ash under conditions which prevail in the water in the vicinity of placement of wood-ash, a ratio of 1:100. The third scenario is the very dilute ratio, which reflects the actual application rate of wood ash in the lake (1:16,000) , simulating the maximum envisaged application rate of 60 t.

In Table 5 we summarize the results of chemical analysis after three leaching experiments, where we added wood-ash to simulated pH 4 Armanda Lake water at different ratios. For each experiment, the analytical data from the supernatant are reported and those concentration can be compared to the calculated values reported in column “ maximum expected”.

This approach has been taken, as solubility of the wood-ash elements would be responding the strong concentration gradient, which will be created with the nearly distilled water of Armanda Lake and the wood-ash (Figure 13). The analytical results from these different wood-ash : water ratios can be compared to the maximum expected. It can be noted that elements of concern, such as metals are generally lower in concentration in the samples analyzed when compared to the concentration which would have been expected if all of the wood-ash had dissolved. The concentrations of Armanda Lake are given for station ML11 and ML43 and a mixture of water from locations (ML11, 43, 44, 51 and 52) used in the 1:100 ratio leaching and neutralization experiment.

In Figure 11, the concentrations of metals in Armanda Lake are plotted for Al, Pb, Mo Cd, Cr, Co, Cu, Ni and for Zn, and those concentrations are reported from the supernatants of the experiment (Table 5). This assessment of the additions of wood-ash along with the maximum expected concentrations shows, that the addition does not alter Armanda Lake measurably, when compared to existing conditions.

A literature review presented in a separate report, summarized soil usage of wood-ash. This review suggested that metal release is not of concern. We confirm this with our work for sediments and acidic water. Most of the wood-ash will sink to the sediment an environment somewhat similar to soil and therefore there is no problem from a metal perspective with the addition of wood-ash. The next step, probably the most difficult step, is the estimation of the amount of wood-ash required to be effective to achieve neutralization of pH depression in Armanda Lake.

6.3 Tonnage of Wood Ash Required for One-Time Treatment Through Lake Ice

The main neutralizing reagents in wood ash are K, Na and, Ca oxides. A fast initial reaction will be provided by potassium oxide, initially increasing the pH in the water column, with remaining neutralizing capacity from the other oxides once these are resident in the Lake sediments. The long-term slower reactants are sodium and

calcium oxide. In a moderate fashion, the wood ash would also be a fertilizer, given that some N-nitrogen is released from the wood ash (Table 5).

The total neutralizing capacity of the wood ash was determined experimentally with 0.1 N sulfuric acid (Table 6). Although in Armanda Lake such strong leaching conditions will never prevail, this value needs to be obtained to define the maximum neutralizing capacity of the material. The value was obtained by making a slurry which was stirred for one minute, let stand for 1 h followed by measurements of pH, Em, conductivity, acidity and alkalinity. The water was decanted until the pH of the 0.1N H₂SO₄ stayed stable. Within 2 h or after the second decant cycle the water reached a pH 6.2 from initially a value 1.0. Clearly, alkalinity was released very fast under those conditions. After 5 decant cycles the end of the experiment was reached, where a total alkalinity release of 27,736 mg/L of CaCO₃ equivalent had taken place.

Although we would like to achieve a pH value of 6.0 in Armanda Lake, we have to understand the interaction between acidity and pH to effectively bring about a pH increase. Any neutralization reaction will not only be the result from consumption of hydrogen ions but also by neutralizing acidity. The metal acidity will consume OH⁻ ions forming hydroxides.

In addition to these two requirements to achieve neutralization the reaction dynamics have to be considered. We know the wood ash contains fast reacting neutralization capacity (Potassium oxide) and slower reacting components with sodium and calcium oxide. We therefore need to determine how pH and acidity interact, in order to select the appropriate estimator for wood ash addition.

In Figure 11 we have plotted the results of a series of experiments where wood ash was added to water with a range of acidity values and a range of ratios of liquid to solid. These different ratios would of course exist in the variability of applications and within the sediment, which has a natural high acidity in the pore-water. Figure 11 shows, that when wood-ash has neutralized to a pH of 6 the solution still contains

acidity , but the pH does no longer increases. This is due to the super-saturation of this condition. If we decrease the ratio of liquid to solid to an acidity equivalent to Mud Lake water, we find that the acidity value is decreased to 10 with a ratio of 1:500 and drops lower with a ratio of 1:250.

The shape of the curve is the same, for the high acidity (0.1 N sulphuric acid) which contains no metals, and the Mud Lake water, which contains metals. The same shape of the curve suggests, that there is a proportionality between pH and acidity, which prevails in dilute (metal free solutions) such as Armanda Lake and in metal containing solutions, such as Mud Lake. Therefore we can use the value of acidity to estimate the neutralizing requirements, integrating metal acidity.

In addition, these experiments gave us some insight into the expected time, with which wood-ash can neutralize under differing acidity values. The high ratio, strong acid conditions reached pH 6 within 1 h, whereas the ratio of 1: 250 required 10 days and finally the lowest ratio required 30 days to reach pH 6. Armanda Lake has an acidity of 26 mg/L CaCO₃ equivalent. The liquid solid ratios of wood ash applied to the lake sediments will cover a range and will vary. Given the lowest ratio needed 30 days to increase to pH 6, adding a scaling factor of at least 2 we expect a pH increase after about 2 months of applying wood ash to Armanda lake .

The conclusion therefore is that in Armanda Lake, the pH will increase easily and using acidity to estimate the amount of neutralizing agent added is the most reliable approach. It should be noted, that addition of too much neutralizing agent would result in undesirable high pH values. Given that Armanda Lake water is essentially pure distilled water with some sulphate and zinc we should be careful not to add too much (Figure 13). In order to arrive at a reasonable ratio of wood ash application for Armanda Lake, we have made the following considerations.

The first step is presented in Table 7 where we give the rational estimation of amount of wood-ash added to Armanda Lake. The volume of the lake is 1 million cubic meter

with an the acidity of 26 mg/L CaCO_3 equivalent. This results in a total acidity of 26,000,000,000 mg/L in Armanda lake. To reach pH 6 the wood-ash had released 16.178 mg/L equivalent within the second decant cycle in the sulphuric acid leaching. The quantity which was released on a weight basis is 485 mg of alkalinity per gram of wood-ash. Thus if we want to reach pH 6 within Armanda Lake, we should add about 54 tones of wood-ash, equivalent to about 10 truck loads (5-6 tones per truck). This would neutralize all of the acidity in Armanda Lake and raise the pH to 6.

However we know , that the total alkalinity in the wood-ash is much higher, than that released after two decant cycles and the pH is increasing in relation to the acidity (Figure 12). We therefore decided to calculate the amount to be added if we assume that all of the alkalinity contained in the wood-ash , 27736 mg /l CaCO_3 equivalent is released. This calculation results in a application rate of 16 tones of (3 truck loads) wood ash. A realistic value for application is between the two calculated values, choosing 30 t as the starting point for the neutralisation.

Based on these estimates of the application rate, we set up an experiment to simulate the application rate. We used a ratio simulating 30 t (15 mg : 500 ml) and measured pH increases in the water (Figure 14). After 3 days or 4300 minutes, we had only reached pH 4.5. We therefore increased the amount added following the calculated values, adding maximum of 60 t (30 mg in 500 ml) . After 4 days (5715 min) the pH had reached in the unstirred beaker pH 6.38. This demonstrates practically, that the calculations used to arrive at this ratio were reasonable. We therefore propose to add minimum of 30 t of wood ash increasing the addition to a maximum of 60 t to Armanda Lake. This should allow to control the effect of the additions on pH in the Lake, comparing laboratory tests and theory to the reality in field conditions. In other words, we do not expect to see any major pH increase until we have added 30 t , but after that time, further additions will result in increases.

6.4 Tonnage of Wood Ash Required for Slurry Treatment at Mud Lake Outflow

The practicality of the wood-ash addition to Armanda Lake is limited to the winter time. Although preparations are underway to access Armanda Lake via an ice trail, passable by snowmobile, we can not guarantee weather which will be limiting factor in this option. If access is no longer possible, then we would be left with no option, if we did not consider other alternatives. Therefore, we have considered additional options, such as the addition of a high pH slurry to Mud Lake outflow.

In **Table 8** the results of adding wood-ash to Mud Lake outflow water directly are presented. Firstly nine (9) g in total were added in increments 1, 5, 2, and 1 g, measuring the increase in pH. After the addition of 5 g the pH has raised to 8.6 in 8 minutes. Secondly, when 10 grams are added in one increment, the pH raised much slower, as with a one time addition pH 7 was reached within one minute, an increase too fast. However over time both application modes produce a high pH of 10. The experimental results of incremental additions of wood-ash, which would be equivalent to addition directly to the creek, are favorable over bulk additions, which would dump larger (truck loads, as compared to small backhoe loads) at once.

In Armanda Lake the physical conditions are different, as a pH gradient which will be created where the wood ash is dumped at the sediment. During spring run-off good mixing of the water with the wood-ash should reach the desired affect. Practically, we tried to simulate what the effect would be of addition of wood-ash directly to the creek leaving Mud Lake, if access is possible during winter. Spring run-off access will likely not be possible, as the flows increase to dramatically in the narrow channel. However it would be possible to access Mud Lake outflow during the summer months.

During spring run off, as was indicated by Murray Johnson, that access is impossible. We are not too concerned about this problem, as the pH is generally not as low as during the summer time (3.0 to 3.6, Figure 3b). After spring break up the situation can be re-assessed and the treatment option in Mud Lake or even at Mud Lake outflow creek can be considered during the summer months, while the in-situ treatment approach is being implemented.

We simulated therefore a treatment scenario for Armanda Lake, where we add pH 10.7 water to the creek leaving Mud Lake (Figure 15). As a starting pH a value of 5.4 was used (assuming a conservative increase in pH due to the winter application of wood-ash to Armanda Lake) . Using this model result, it appears that we have to treat for at least one entire year. If the winter additions is not sufficient to increase the pH to 6.0 we have defined the parameters for post spring run-off treatment.

It should be remembered, that the assessment does not take into account the sediment addition and its long term effect, which is not to be discounted to be effective. It may be useful to recall further, all the predictions generated by the model was mixing waters with different pH values only and they are producing lower values as measured. We take with this approach as a precaution , as we have made the assumption, that no sediment or other biological buffering capacity is remaining in Armanda Lake, for which we have no evidence.

7.0 Recommended Treatment Approach for Armanda Lake

Our most preferred option is the application of 30 t of wood-ash through the ice directly to Armanda Lake. If the response to the addition is comparable to the experimental results , then we proceed to add 60 t maximum. We have made throughout the experimentation very conservative estimated, leading to the suggested stepwise approach. Field condtions are frequently different than those anticipated by theory and experiments.

The timing is requested, as spring runoff is expected to produce good mixing within Armanda Lake. Access is possible only during the winter time with a acceptable ease. From the aerial photograph of the topography between Mud Lake and Armanda lake (Plate 3), the terrain suggests the difficulties to accessing Armanda Lake during the summer. In the summer Armanda Lake has to be accessed via Lena Lake through higher grounds.

We have prepared a trail to haul with snow-machines and buggies wood-ash (covered with tarps) from the shores of Mud Lake (close to gravel pit) to Armanda Lake. The proposed trail and dumping locations are given in [Map 3](#). Holes will be cut through the ice large enough to dump the wood-ash directly into the water. All operational aspects have been addressed with Murray Johnson from Ear Falls. He has been instructed with respect of the care (respiratory protection, overalls and gloves) with which the woodash has to be handled. This option can be implemented as soon as the ministry approves the release of the wood-ash from the land fill site in Ear Falls.

A further reason that this option is preferred, because it represents the first step, the most logical step. Most of the wood-ash will be distributed over the sediment in the lake during spring run-off passively, when the physical forces in the lake are strongest for mixing water. This provides the treatment and fertilization of the water for spring algae bloom, which in turn will assist in increasing buffering capacity of the drainage basin.

The least preferred option, economics notwithstanding, is addition to Mud Lake outflow, because it will be a wasteful approach, as there is little control over the fate of wood-ash between Mud Lake and Armanda Lake ([Plate 3](#)). If any of the wood-ash, delivered as slurry or delivered directly, accumulates in the muskeg, high pH will develop in certain locations, which is as damaging as low pH. As the wood-ash particles have the tendency to sink to the sediment, the treatment is most effective at the sediment water inter-phase.

8.0 Monitoring Program

The effect of the wood-ash addition to Armanda Lake will be monitored at several stations in the lake. The locations where the wood-ash is placed will be monitored and compared to the results obtained in the experiments. During the wood-ash application,

Boojum staff will determine further monitoring stations, which will be selected based on the currents under the ice. Monitoring will consist of determinations of field and

laboratory parameters (pH, Eh , conductivity and acidity) . Samples will be send for chemical analysis if any of the monitoring parameters are changing sufficient to warrant detailed analysis. It is expected that at the locations were the wood-ash is placed, the pH will increase dramatically immediately and dependant on the currents, pH changes should follow the currents. The fist 3 truck load applications will be supervised by Boojum staff in the field, so that the predictions made based on the laboratory work can be confirmed. We anticipate to report verbally to the ministry, when the first truck loads have been applied.

9.0 References

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Table 1a:Chemistry of Water Samples from Armanda Lake

Date	Field pH	Acidity mg/L as CaCO ₃	SO ₄ mg/L	Zn mg/L	Fe mg/L
Historic Chemistry					
5-Mar-87	6.79		3	0.1	0.01
Location ML11					
20-Mar-95	6.40	4.1	93	0.55	0.71
20-Feb-96	6.74	1.8	97	0.89	1.17
10-Mar-00	5.41*	19.9	81	1.2	0.14
31-Dec-00	4.13*	25.9	126	2.4	1.4
1-Feb-01	5.16*	16	96	1.7	0.67
Location ML43					
20-Feb-96	7.15	1.5	97	0.93	1.17
10-Mar-00	5.53*	16.1	93	1.4	0.13
31-Dec-00	3.99*	25.7	129	2.4	1.5
1-Feb-01	3.88*	27.4	135	2.6	1.4
Location ML 44					
10-Sep-97	5.77	13.3	67	1.01	<.004
26-Mar-98	5.60*	35.5	105	1.2	0.09
10-Mar-00	5.50*	16.4	72	1.1	0.22
31-Dec-00	3.99*	26.1	132	2.4	1.5
1-Feb-01	3.91*	28.1	nm	nm	nm

* Lab pH. nm: not measured.

Table 1b: Chemistry of Water Samples form Lena Lake

Date	Field pH	Acidity mg/L as CaCO ₃	SO ₄ mg/L	Zn mg/L	Fe mg/L
location NE1					
20-Mar-95	6.11	0.7	2.6	0.02	0.11
20-Feb-96	6.22	0.9	2.7	0.17	0.38
5-Sep-96	7.53	6.5	2.3	0.02	0.25
10-Sep-97	6.87	2.8	2.1	0.06	<0.04
7-Dec-99	5.69	17.5	2.5	0.02	0.16
10-Mar-00	no sample collected				
31-Dec-00	7.00	5.8	2.5	0.02	0.31
1-Feb-01	6.92*	8.7	2.4	0.014	0.3
Location NE2					
20-Mar-95	no sample collected				
20-Feb-96	6.24	0.1	2.31	0.12	0.66
5-Sep-96	no sample collected				
10-Sep-97	no sample collected				
7-Dec-99	5.94	8.6	2.3	0.01	0.15
10-Mar-00	5.93	11.3	2.6	0.04	0.07
31-Dec-00	7.02	5.8	2.6	0.01	0.29
1-Feb-01	5.99*	7.5	2.3	0.02	0.28

* Lab pH.

Table 2: Surface Runoff for Drainage Basins

Drainage Basin	Land Area ha	Lake Area ha	Total Area ha	Total Runoff		Measured 14-Aug-92 to 1-Feb-01			
				m3/y	L/sec	Max L/sec	Min L/sec	Avg L/sec	N
Armanda Lake	198	54	252	639,300	20	-	-	-	-
Lena Lake	176	25	200	525,500	17	-	-	-	-
Mud Lake	155	13	168	449,400	14	35	2	13	16
Total Drainage Basin	529	91	620	1,614,200	51	-	-	-	-

Lake runoff: 175 mm/y precipitation

Land runoff: 275 mm/y precipitation

Error within estimate: +/- 1 ha

Table 3: Comparison of Water Chemistry

Location	pH			Em (mv)		
	31-Dec-00	1-Feb-01		31-Dec-00	1-Feb-01	
	measured	measured		measured	measured	
	4-Jan-01	5-Feb-01	12-Feb-01	4-Jan-01	5-Feb-01	12-Feb-01
ML52	no sampling	4.043	4.009	no sampling	378	396
ML43	3.99	4.093	3.877	398	387	364
ML 44	3.99	4.072	3.901	386	366	369
ML51	no sampling	4.451	4.369	no sampling	361	372
ML11	4.13	5.056	5.160	387	296	281
ML30	no sampling	4.228	5.258	no sampling	345	244
ML10		4.364	4.428		387	454
NE1		6.967	6.922		236	286
NE2	7.02	6.791	6.847	202	202	236
Location	Conductivity (us/cm)			Acidity (mg/l)		
	31-Dec-00	1-Feb-01		31-Dec-00	1-Feb-01	
	measured	measured		measured	measured 5-Feb-01	
	4-Jan-01	5-Feb-01	12-Feb-01	4-Jan-01		
ML52	no sampling	332	358	no sampling	25.6	
ML43	263	369	368	25.7	27.4	
ML 44	250	346	375	26.1	28.1	
ML51	no sampling	327	332	no sampling	19.3	
ML11	210	238	242	25.9	16	
ML30	no sampling	326	320	no sampling	24.7	
ML10		293	295		19.8	
NE1		60.5	58	5.8	8.7	
NE2	42	59.7	60	5.8	7.5	

Table 4: Example calculation of pH following mixing of two solutions

Mud Lake + Armanda			
Mixed pH: OUTPUT		4.451	
Mud L. flow (31-Mar-00)	6.0 L.s ⁻¹		
pH of Mud lake	2.70		
Input Vol. over month in Mud Lake	16,070,400 L	V ₁	
Initial pH of Armanda lake	5.41		
Vol. of Armanda lake	1,000,000,000 L	V ₂	
Mud Lake [H+]	2.00E-03 M	[H ⁺] ₁	
Mud Lake [OH-]	5.01E-12 M	[OH ⁻] ₁	
Armanda Lake [H+]	3.89E-06 M	[H ⁺] ₂	
Armanda Lake [OH-]	2.57E-09 M	[OH ⁻] ₂	
Solution mix before equilibrium			
[H+] mix = [H+] ₁ * V ₁ +[H+] ₂ * V ₂ / (V ₁ +V ₂)		3.539E-05 M	
[OH-] mix = [OH-] ₁ * V ₁ +[OH-] ₂ * V ₂ / (V ₁ +V ₂)		2.530E-09 M	
Equilibrium: x moles of H+ and OH- react to form H ₂ O			
{[H+] _{mix} - x} * {[OH-] _{mix} - x} = 1 X 10 ⁻¹⁴ or 0 = Ax ² - Bx + C - (1 x 10 ⁻¹⁴)			
Quadratic formula: y = Ax ² +Bx +C			
A	1.000E+00		
B	-3.539E-05		
C	7.952E-14		
Solving for x			
B ² -4AC =	1.25206E-09	positive, therefore 2 solutions	
Sol'n (i): -C - sqrt(B ² -4AC) / 2A	2.247E-09	for x	Real Solution
Sol'n (ii): -C + sqrt(B ² -4AC) / 2A	3.539E-05	for x	Not viable, not enough H ⁺ left
[H+] _{eq} =[H+] _{mix} -x	3.538E-05	= [H ⁺] _{eq}	
[OH-] _{eq} =[OH-] _{mix} -x	2.826E-10		
1E-14 = [H ⁺] _{eq} x [OH ⁻] _{eq}			
Mixed pH: OUTPUT		4.451	

Table 5 : Elemental Concentration in Wood Ash Slurries

Parameter (mg/L)	ML11	ML43	Mixed ML11, 43, 44, 51, 52	Total [M] in Wood Ash (ug/g) _{dry}	Wood Ash in DH ₂ O (20g in 100mL for 7days) (1:5)		Wood Ash in mixed Armanda L. water (3.6g in 400mL for 10days) (1:100)		Wood Ash in pH 4 solution (30mg in 500mL for 7 days) (1:16000)	
	Report by SRC			Report by SRC	report by SRC	Maximum expected	report by SRC	Maximum expected	report by SRC	Maximum expected
Al	0.38	0.62	0.54	1.9	8.1	0.38	0.012	0.0171	0.007	0.00011
Ba	0.035	0.046	0.042	840	0.026	168	0.069	7.56	0.027	0.0504
Be	<0.001	<0.001	<0.001	0.5	0.001	0.1	<0.001	0.0045	<0.001	0.00003
B	0.008	0.007	0.007	80	2.8	16	0.33	0.72	0.036	0.0048
Cd	<0.001	<0.001	<0.001	2.3	0.005	0.46	<0.001	0.0207	<0.001	0.000138
Ca	29	36	35	81100	5.4	16220	31	729.9	4.7	4.87
Cr	<0.001	<0.001	<0.001	4.8	0.058	0.96	0.005	0.0432	<0.001	0.000288
Co	0.01	0.015	0.014	13	0.001	2.6	<0.001	0.117	<0.001	0.00078
Cu	0.066	0.17	0.075	33	0.021	6.6	0.002	0.297	0.002	0.00198
Fe	0.67	1.4	0.4	6300	0.17	1260	0.011	56.7	0.002	0.378
Pb	0.002	0.006	0.003	4	0.002	0.8	0.002	0.036	<0.002	0.00024
Mg	4.8	6.2	5.9	7100	0.1	1420	4	63.9	0.6	0.426
Mn	1.8	2.5	2.3	3700	0.019	740	0.007	33.3	0.041	0.222
Mo	<0.001	<0.001	<0.001	1.6	0.4	0.32	0.012	0.0144	<0.001	0.000096
Ni	0.002	0.002	0.002	8.9	0.001	1.78	<0.001	0.0801	<0.001	0.000534
P	<0.01	<0.01	<0.01	2500	0.11	500	0.02	22.5	0.03	0.15
K	1.5	1.6	1.7	13400	1700	2680	91	120.6	5.9	0.804
Si	3	3.5	3.5	-	25	-	9.7	-	0.52	-
Ag	<0.001	<0.001	<0.001	6800	0.001	1360	<0.001	61.2	<0.001	0.408
Na	1.7	2	1.9	1700	83	-	9.4	-	1.2	-
Sr	66	0.082	0.078	260	0.036	52	0.15	2.34	0.022	0.02
S	32	45	42		-	0	56	0	3.4	0.00
Ti	0.001	<0.001	<0.001	480	0.001	96	<0.001	4.32	<0.001	0.0288
V	<0.001	<0.001	<0.001	12	0.03	2.4	0.002	0.108	<0.001	0.00072
Zn	1.7	2.6	2.3	590	0.065	118	<0.005	5.31	0.01	0.0354
Zr	<0.001	<0.001	<0.001	2.4	0.001	-	<0.001	-	<0.001	-
NH ₃ -N	-	-	-	-	0.34	-	0.08	-	0.3	-
(NO ₂ + NO ₃)-N	-	-	-	-	3.6	-	0.34	-	0.05	-
TKN	-	-	-	-	1.6	-	0.42	-	0.68	-
pH	5.16	3.877	4.006	-	11.535	-	9.24	-	6.78	-
Em (mv)	281	364	389	-	-65	-	154	-	194	-
Cond (us/cm)	242	368	331	-	4996	-	567	-	64.3	-
Alkalinity	3.7	0	0	-	975.3	-	45.6	-	6.5	-
Acidity	16	27.4	25.8	0	0		0		8.8	

Table 6: Total Alkalinity Capacity of Wood Ash Collected at Ear Falls South Bay

Decant Cycle	0.1N H ₂ SO ₄ added to 10 g wood ash (mL)	Time Measured after addition (hour)	React condition	pH	Em (mv)	Cond (us/cm)	Acidity (mg/L)	Remaining Alkalinity (mg/L)	Total Alkalinity (mg/L)	Cumulative Alkalinity (mg/L)
0.1N H ₂ SO ₄				1.04	459	23200	5098.2	0	0	0
0	100	1	Stir	7.48	276	6360	117.7	682	5663	16178
1	100	1	Stir	6.65	376	3550	207.1	453	5344	
2	100	1	Stir	6.26	367	2880	133.3	206	5171	
3	100	1	Stagnant	2.73	338	3730	808	0	4290	11558
4	100	1	Stir	1.82	373	7260	2653.4	0	2445	
5	100	1	Stir	1.49	506	12870	3521.8	0	1576	
		4	Stagnant	3.66	306	3000	734.1	0	4364	
		5208		3.87	336	3360	274.8	0	4823	
Total										27736

Table 7: Estimated Amonut of Wood Ash Needed for Amanda Lake

Total Volume of Armanda Lake		m3	1,000,000
Acidity of Armanda Lake		mg/L	26
Total Acidity of Armanda Lake		mg/L	26,000,000,000
Alkalinity generated by wood-ash in water	to reach pH 6.0 (after 2 nd decant cycle, see Table 6)	mg/L	16178
Alkalinity generated by per gram wood ash		mg	485
Amount of Wood Ash needed for Amanda Lake		ton	54
Total alkalinity generated in water by wood ash	when pH stays stable (after 5 th decant cycle, see Table 6)	mg/L	27736
Total alkalinity generated by per gram wood ash		mg/g	1664
Amount of Wood Ash needed for Amanda Lake		ton	16

Table 8: Using Wood Ash to Treat Middle Mud Lake Water

9 g wet wood ash + 100ml MML water (adding wood ash in 4 times)					10g wet wood ash + 100ml MML water (adding in one time)				
Wood Ash added (g)	Reaction condition	Reaction Time (min)	pH	Em	Wood Ash added (g)	Reaction condition	Reaction Time (min)	pH	Em
0	stagnant	0	3.25	471	0	stagnant	0	3.22	419
1	stir for 20 seconds	2	3.94	397	10	stir for 20 seconds	1	7.43	81
	stagnant	3	4.15	367		stagnant	3	7.56	108
5	stir for 20 seconds	4	6.32	147		stagnant	26	7.78	211
	stagnant	5	6.96	34		stir for 20 seconds	27	9.33	120
		6	7.51	-24		stagnant	28	9.41	109
		7	8.33	-34			31	9.49	131
		8	8.64	81			46	9.55	149
2	stir for 20 seconds	10	9.66	33			56	9.48	141
	stagnant	11	9.79	-5		1091	10.35	100	
		12	9.88	-12		ongoing			
1	stir for 20 seconds	14	10.19	26					
	stagnant	15	10.18	29					
		17	10.17	80					
		75	10.01	87					
		1105	10.71	100					
ongoing									

Fig.1: Middle Mud Lake, MML
Seasonal Iron Concentration

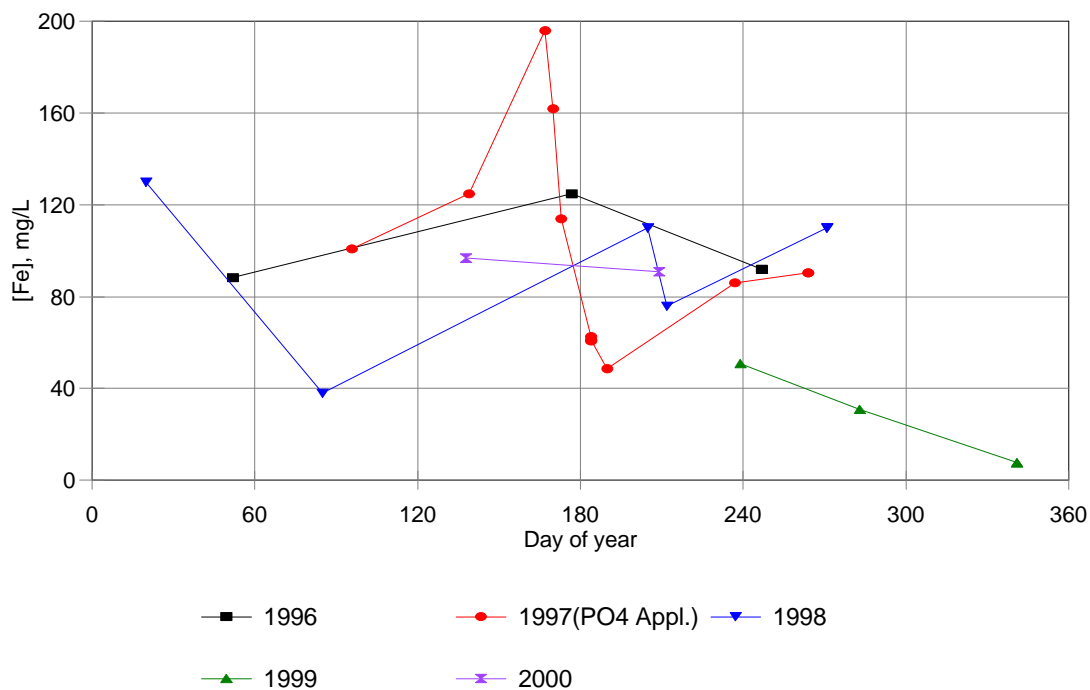
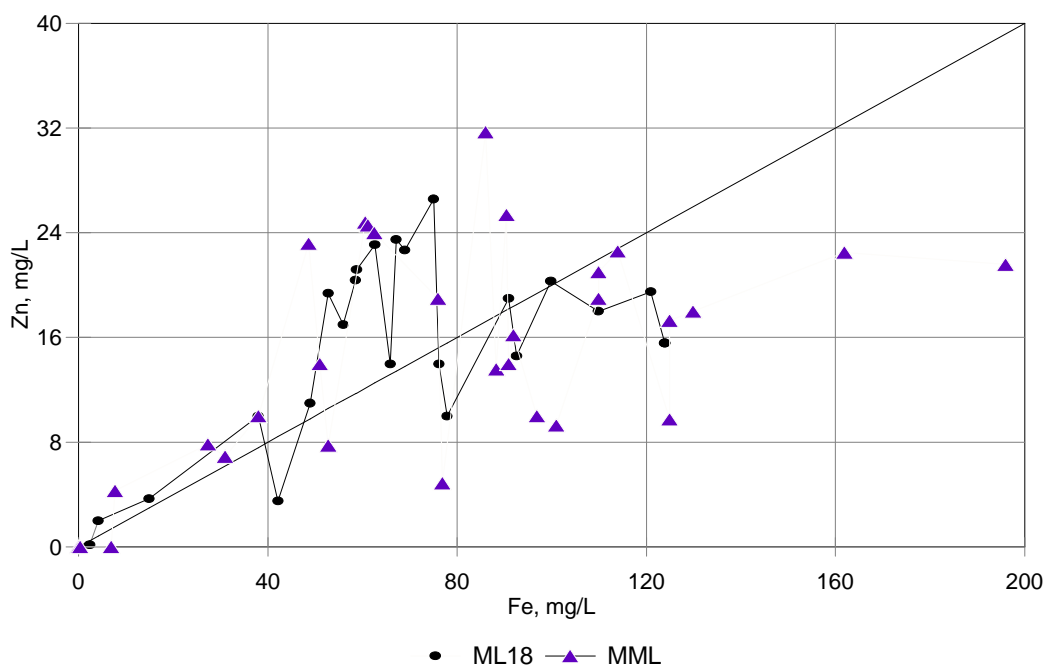


Fig.2: ML18 and MML
Zinc versus Iron



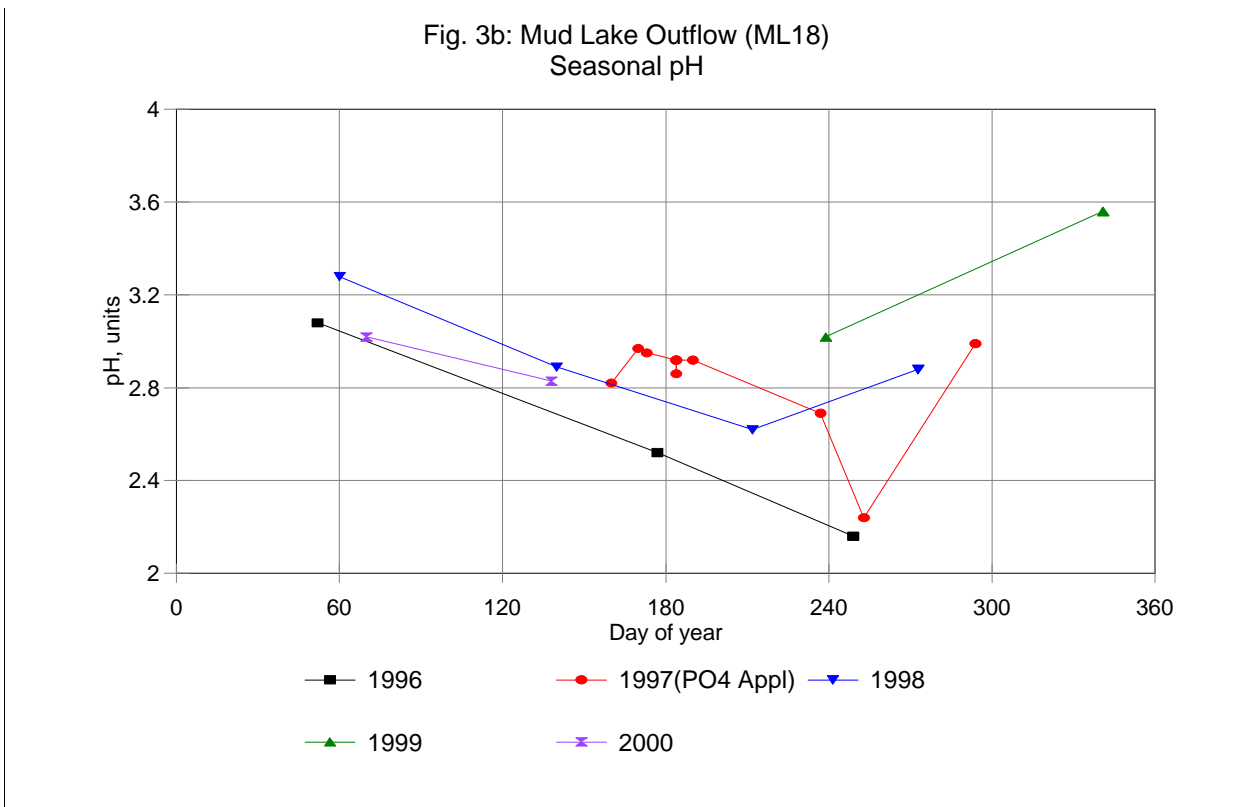
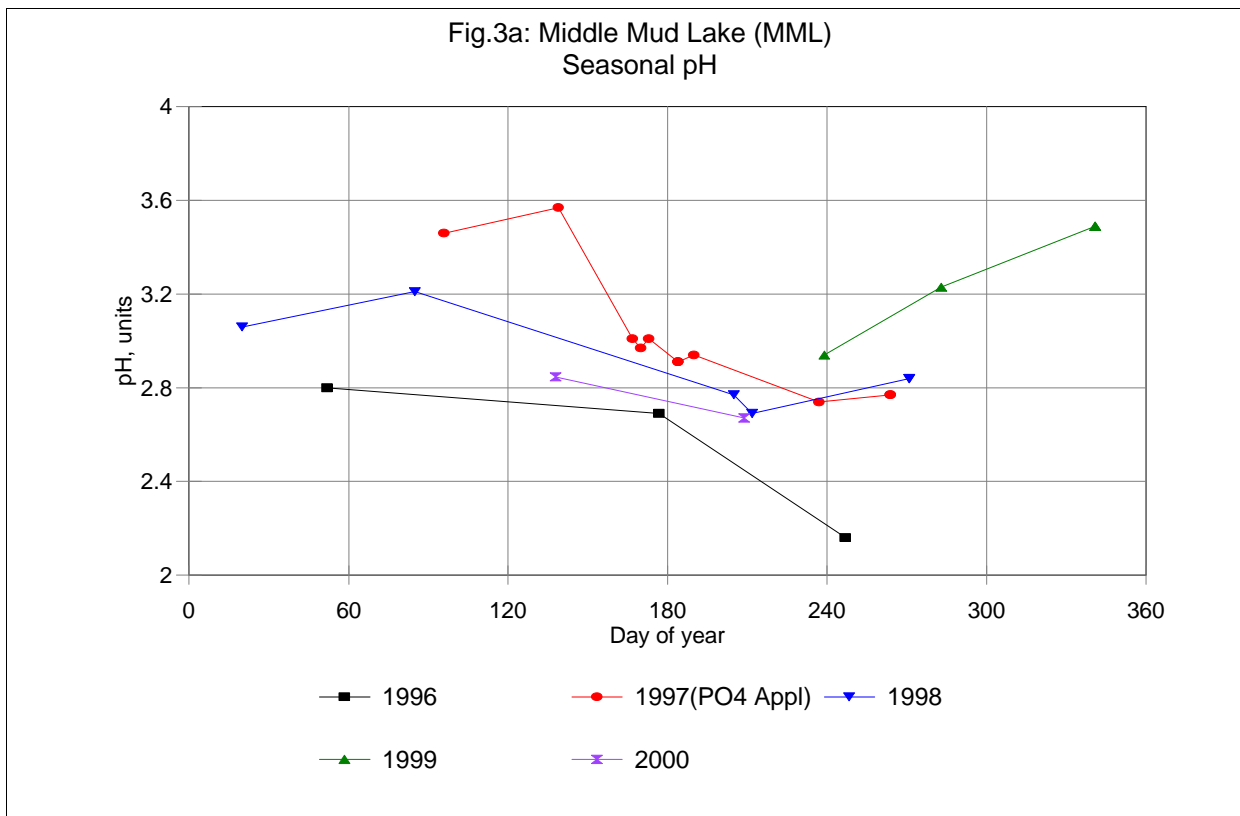


Fig 4: Armanda Lake
[Zn] vs Time

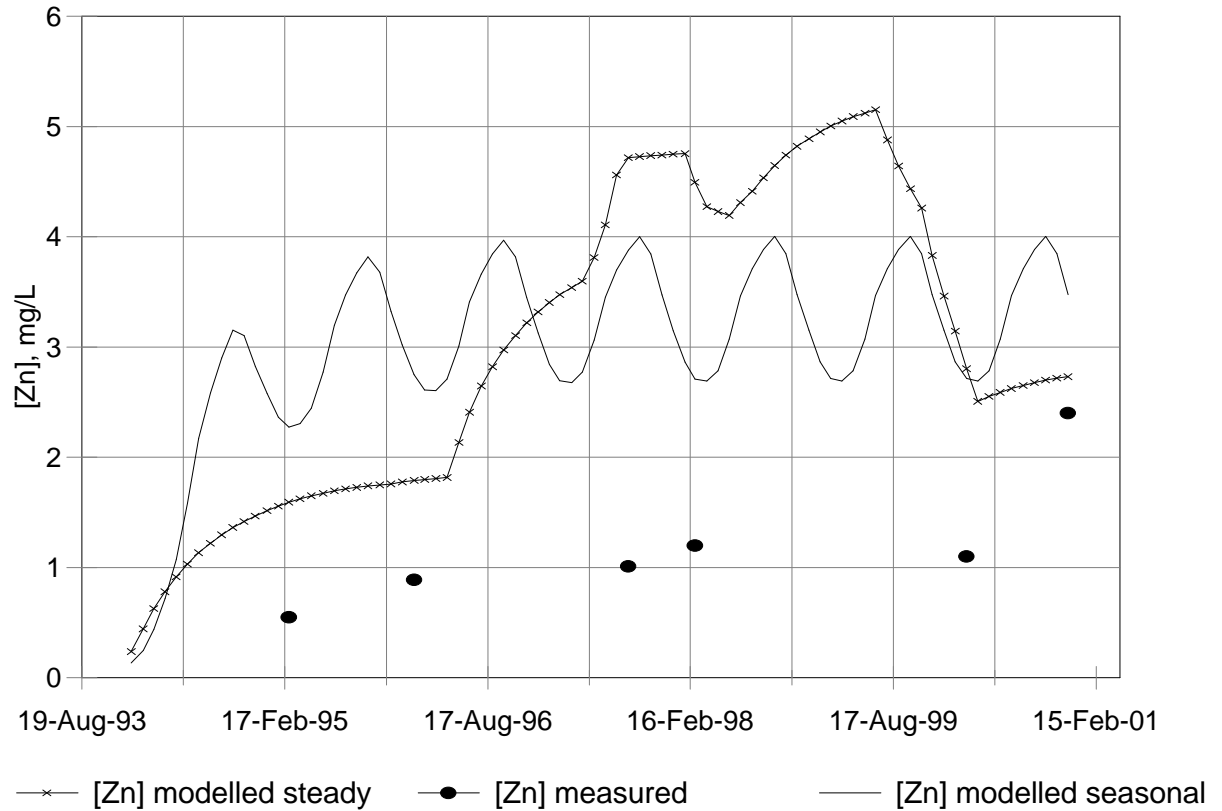


Fig. 5a: Middle Mud Lake, MML
Seasonal Zinc Concentration

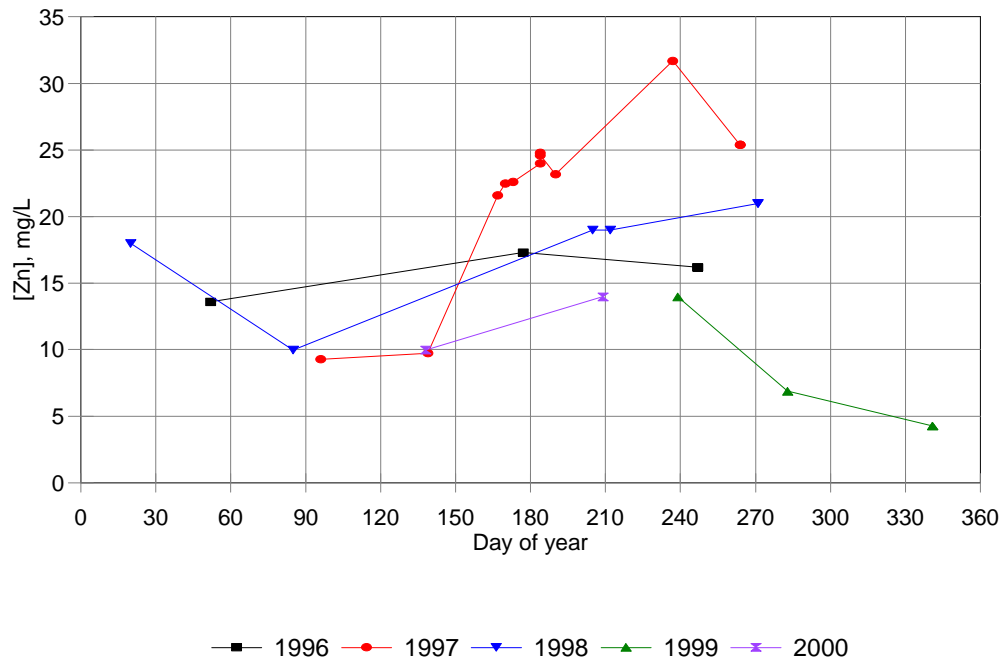


Fig. 5b : Mud Lake Outflow, ML18
Seasonal Zinc Concentration

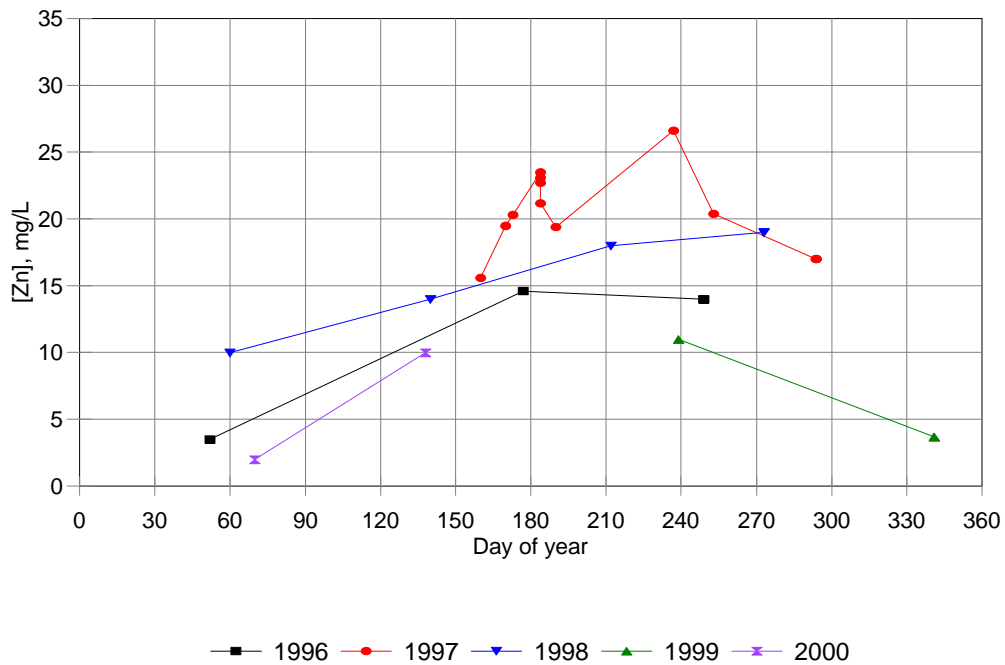


Fig. 6a : Comparison of Field and Lab pH in C1, and C8 (1989-2000)

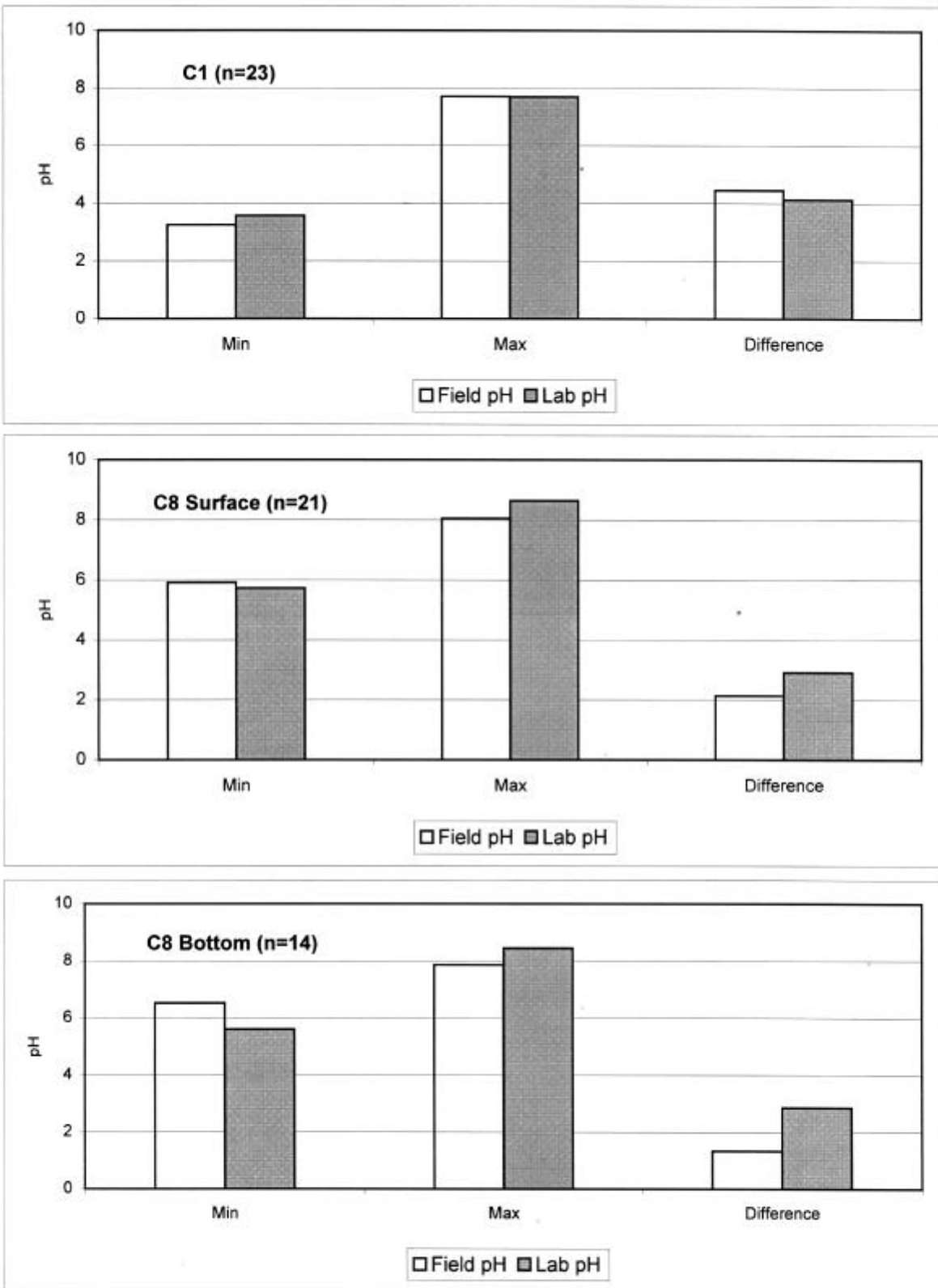


Fig. 6b: Comparison of Field and Lab pH in C11, Armanda and Lena Lakes (1989-2000)

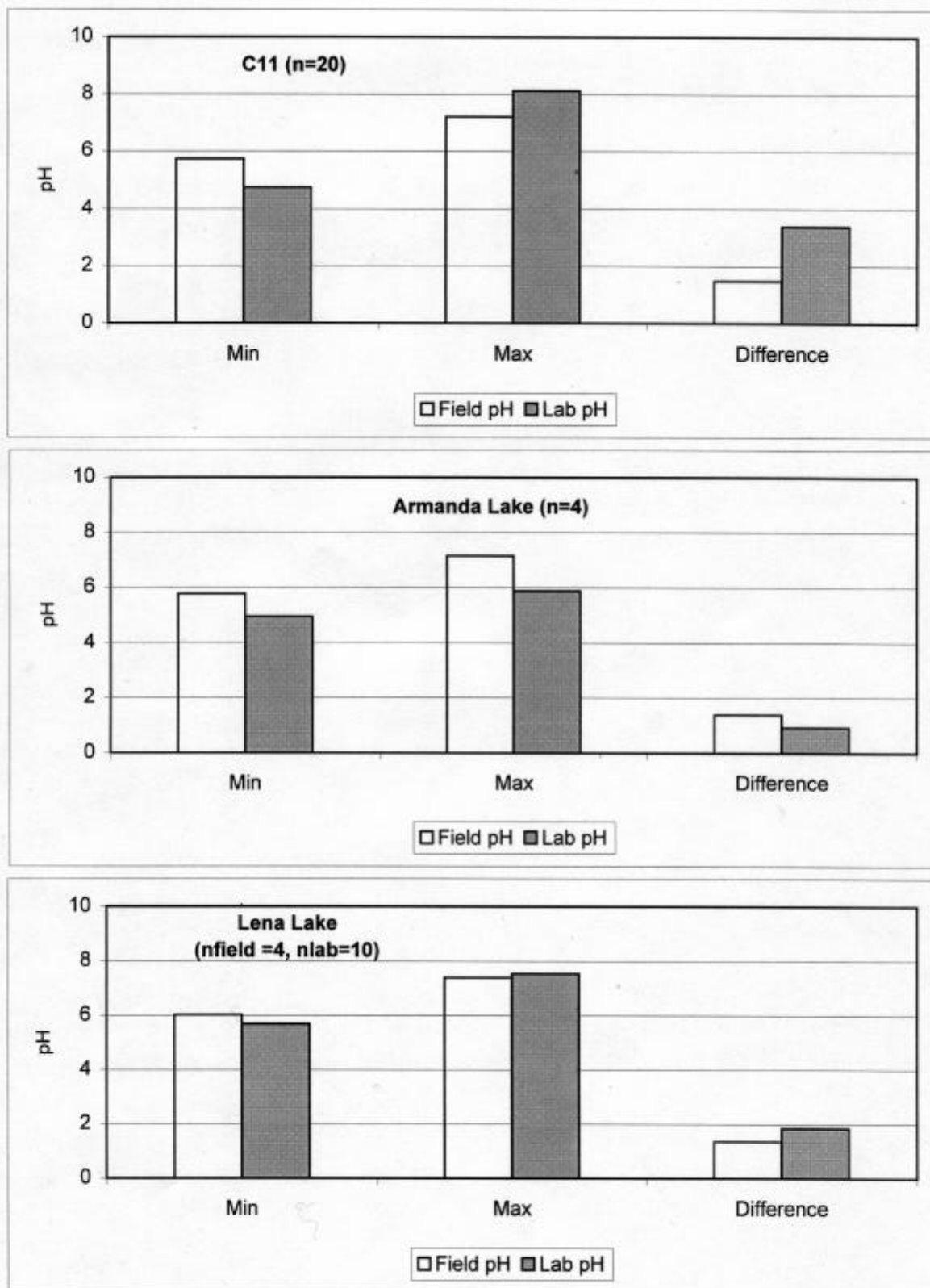


Fig. 7: Armanda L- Beaver Dam Intact
Initial pH 5.41: ML18 Input pH 2.7

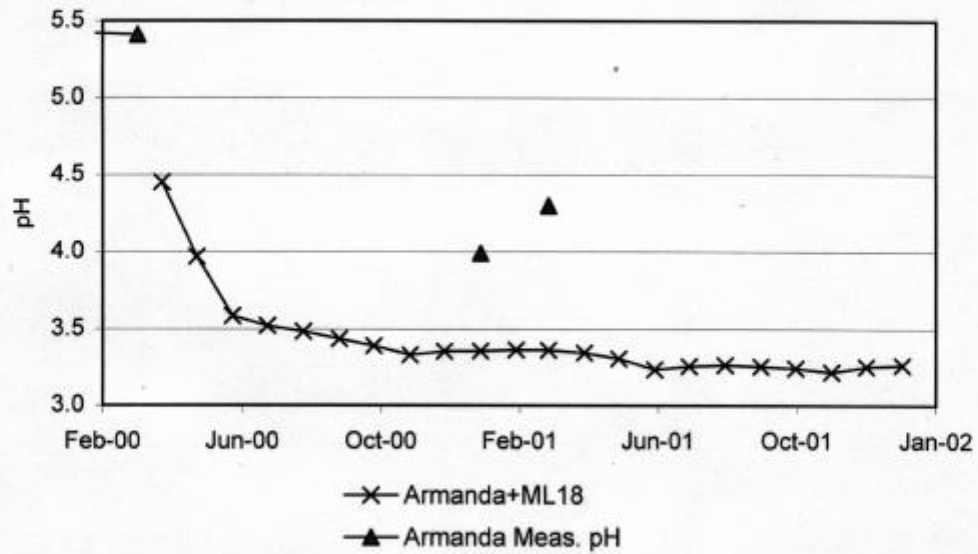


Fig. 8: Armanda L.- Beaver Dam Drained
Initial pH 5.41: ML18 Input pH 2.7: Drained June, 2000

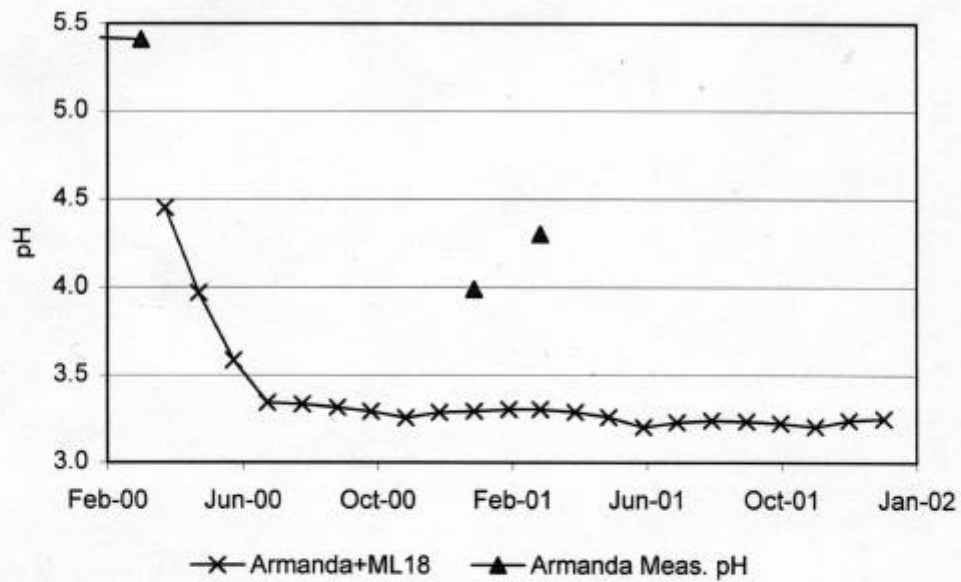


Fig. 9: Armanda L. - Slower Acidification
Initial pH 6.4 : ML18 pH 4.0

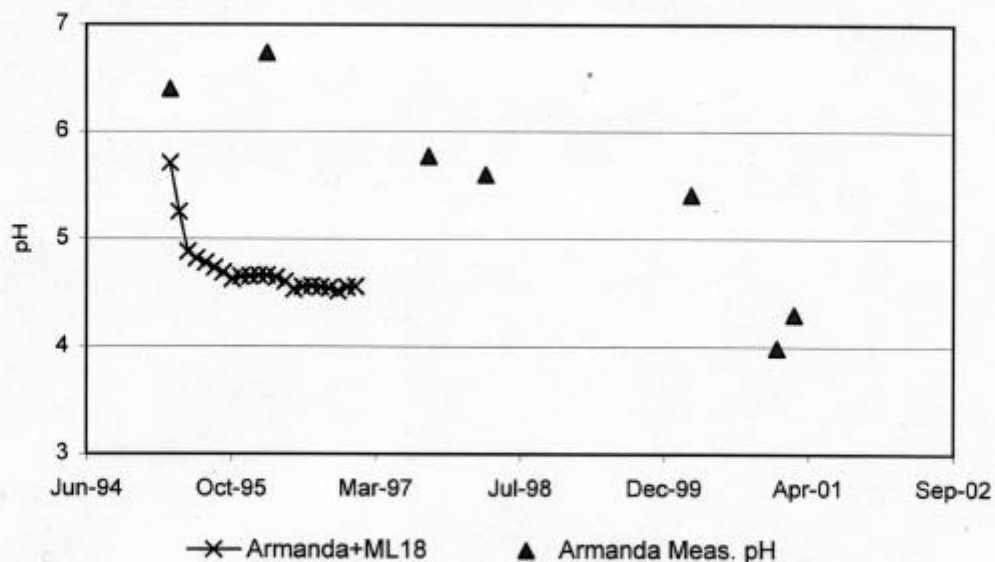


Fig. 10: Armanda L. - Rapid Acidification
Initial pH 6.4 : ML18 Input pH 2.7

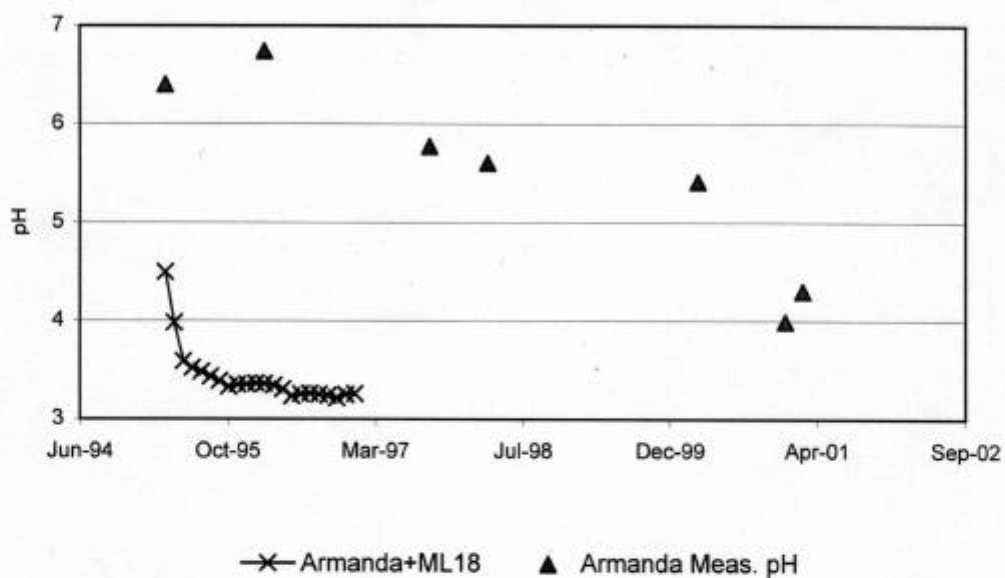
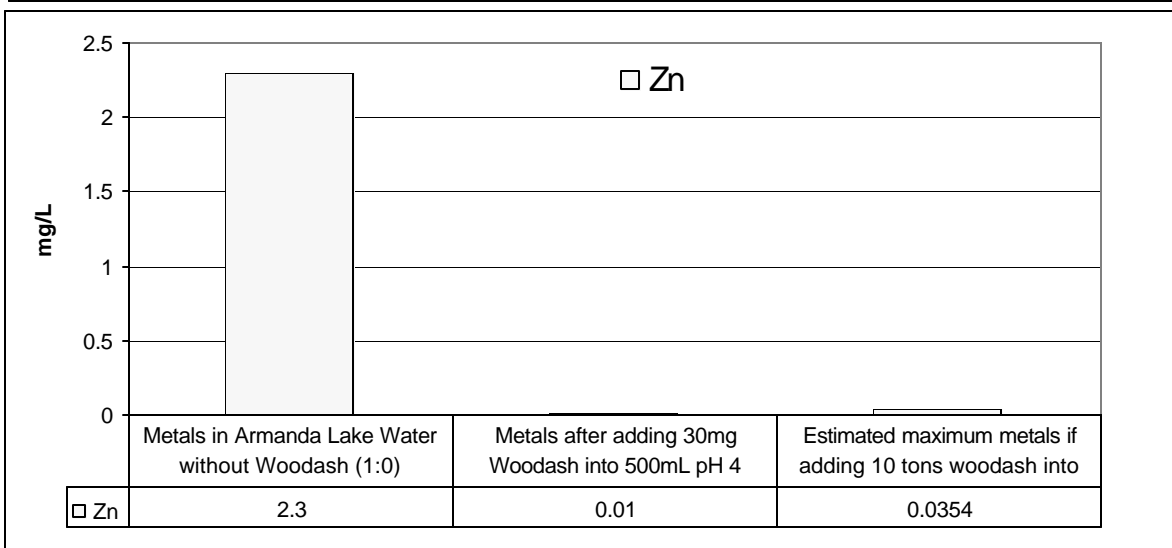
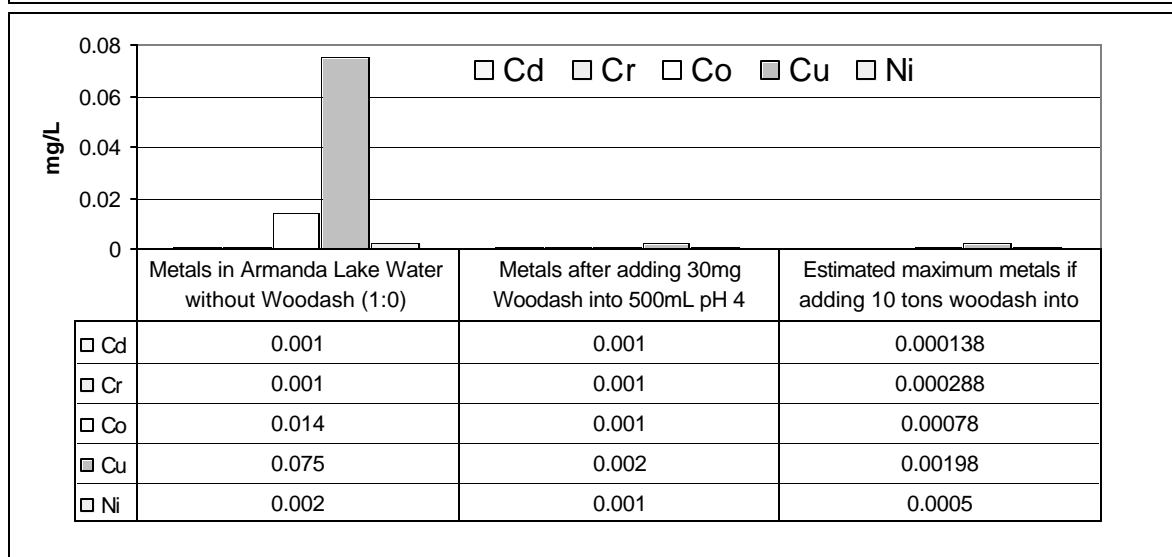
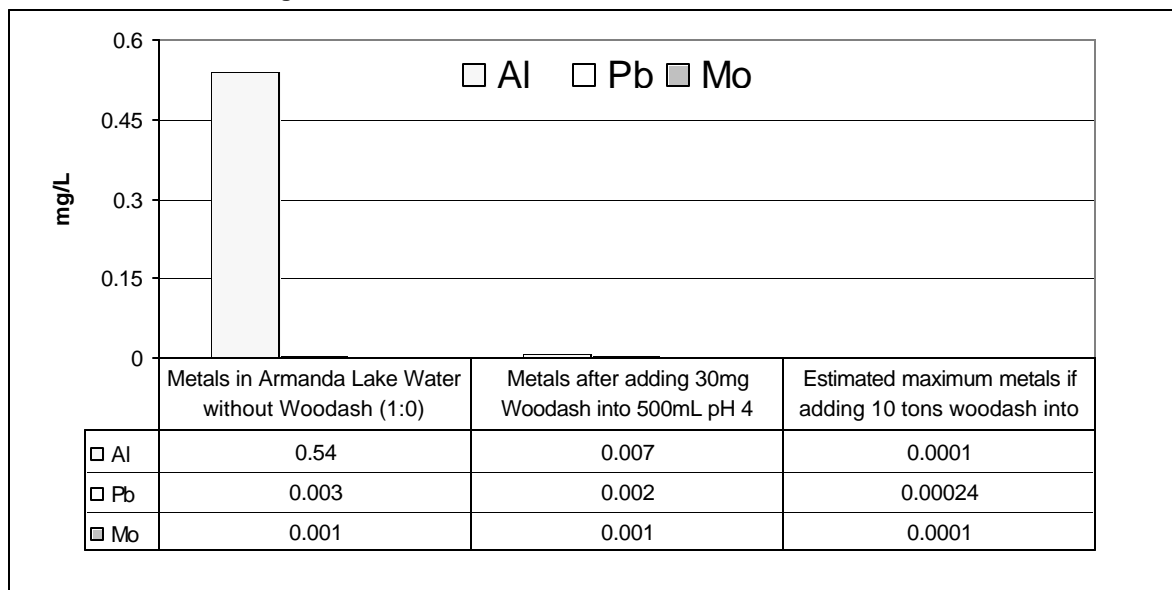


Figure 11: Metals in Armanda Lake before and After Wood Ash Addition



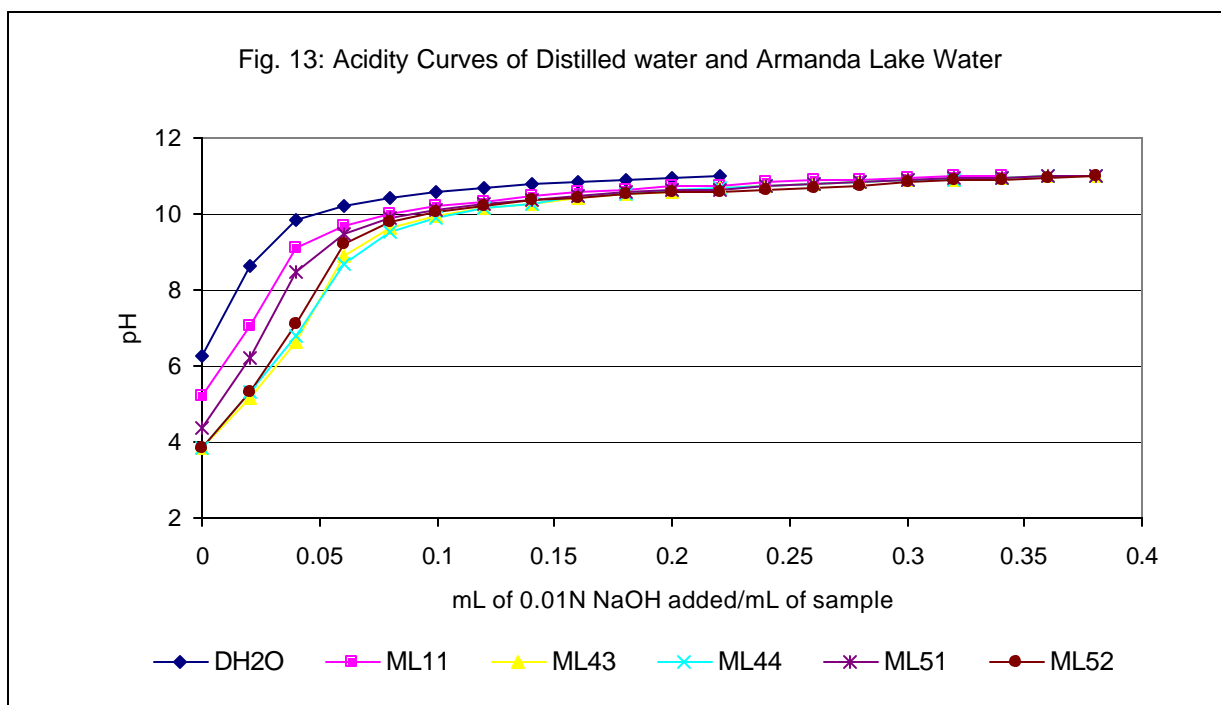
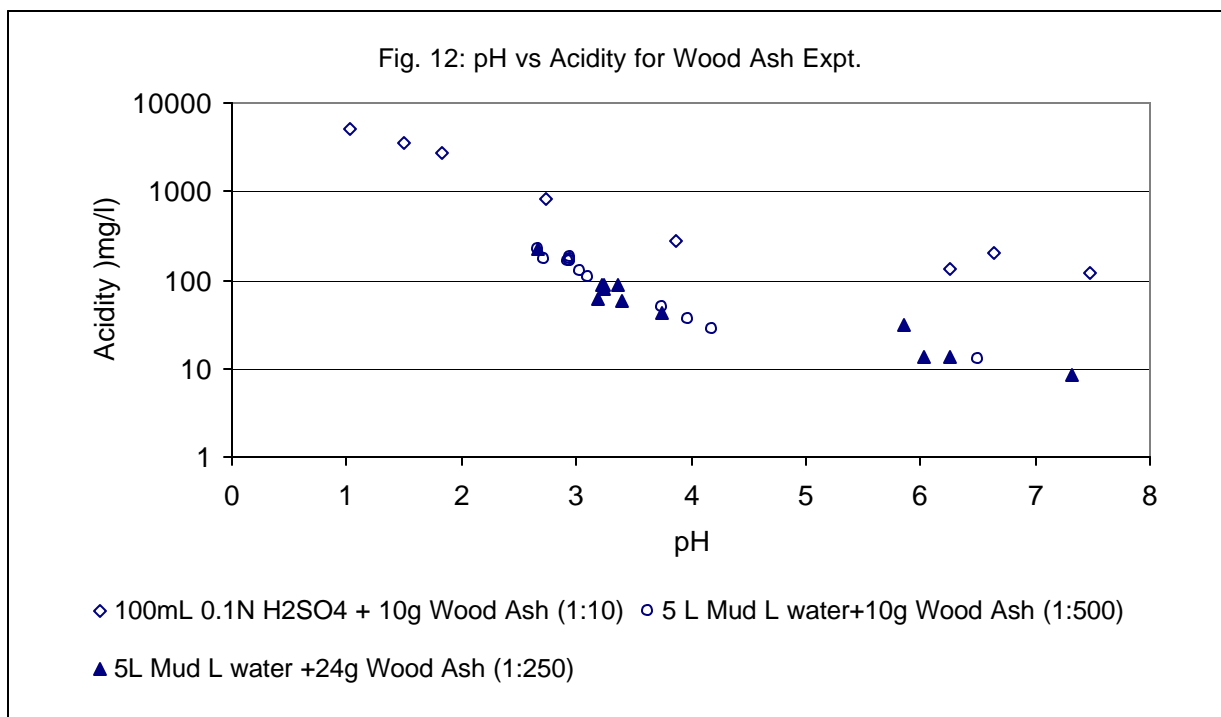


Fig. 14: Practical Dosage of Wood-ash for Armanda Lake

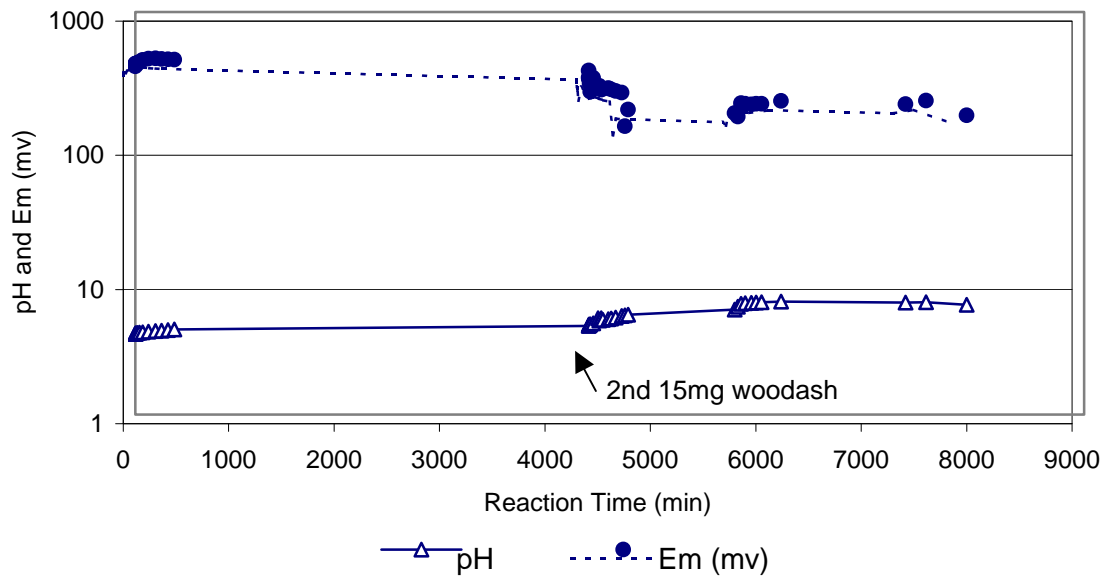
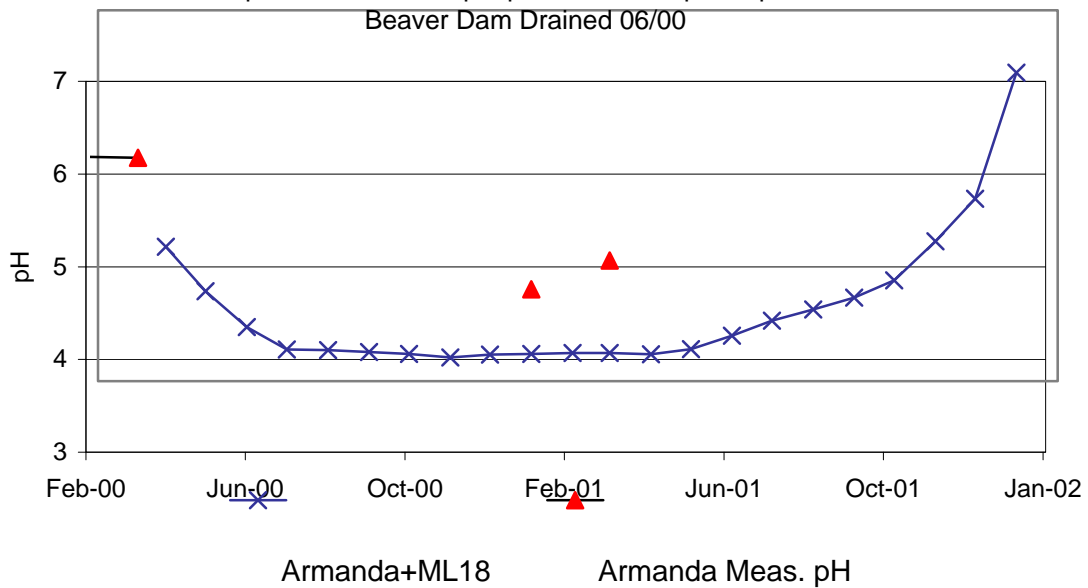
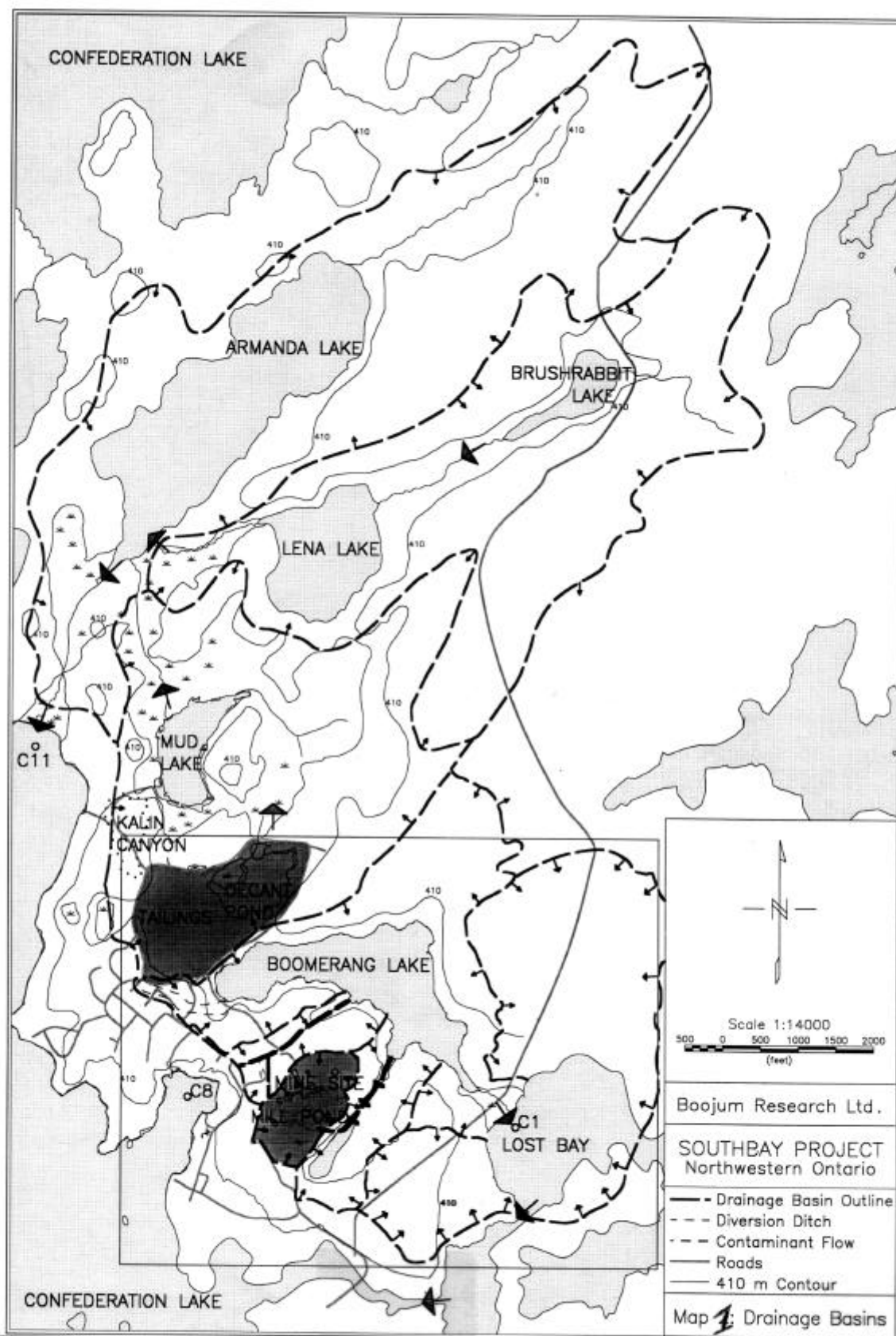
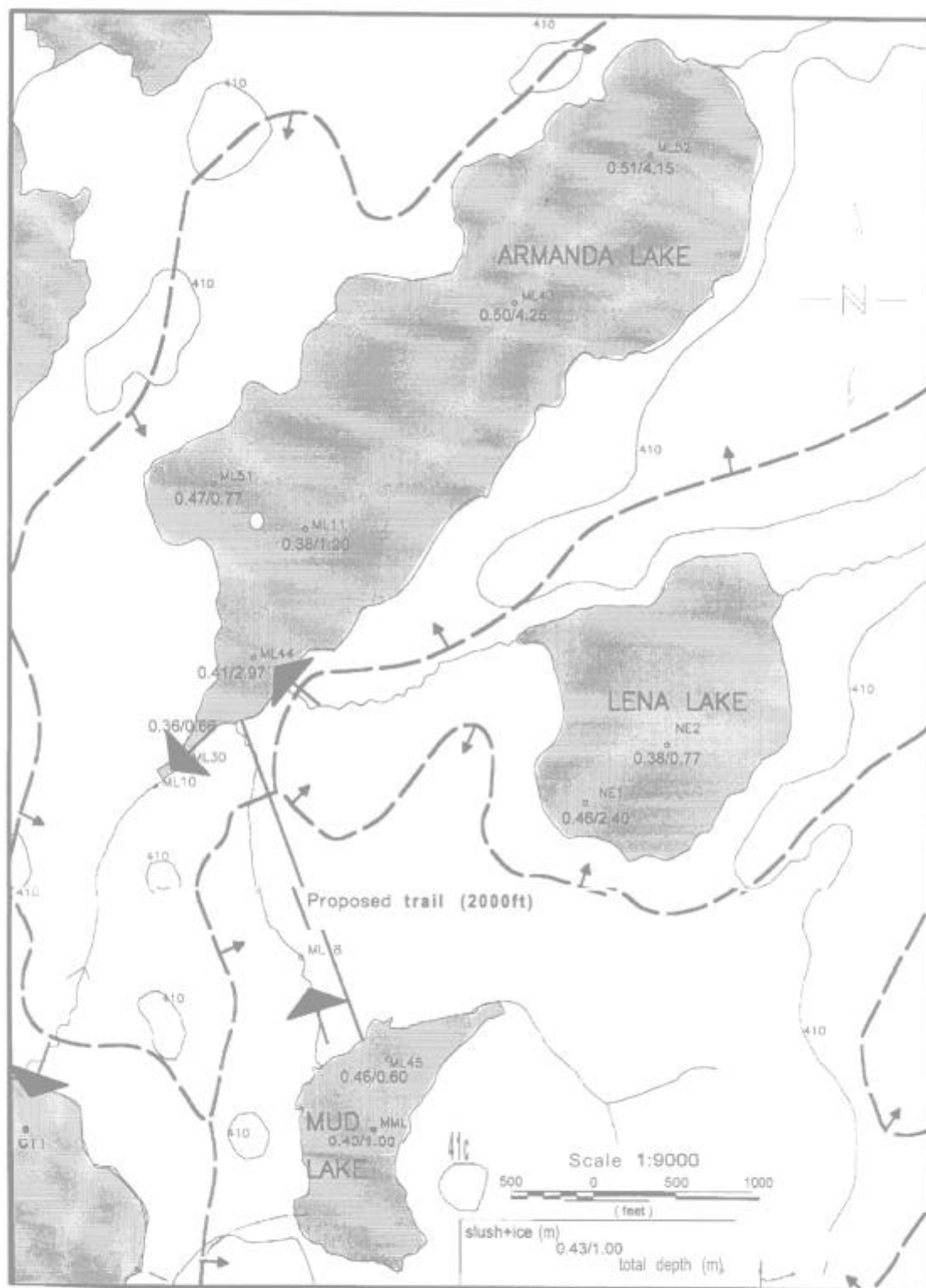


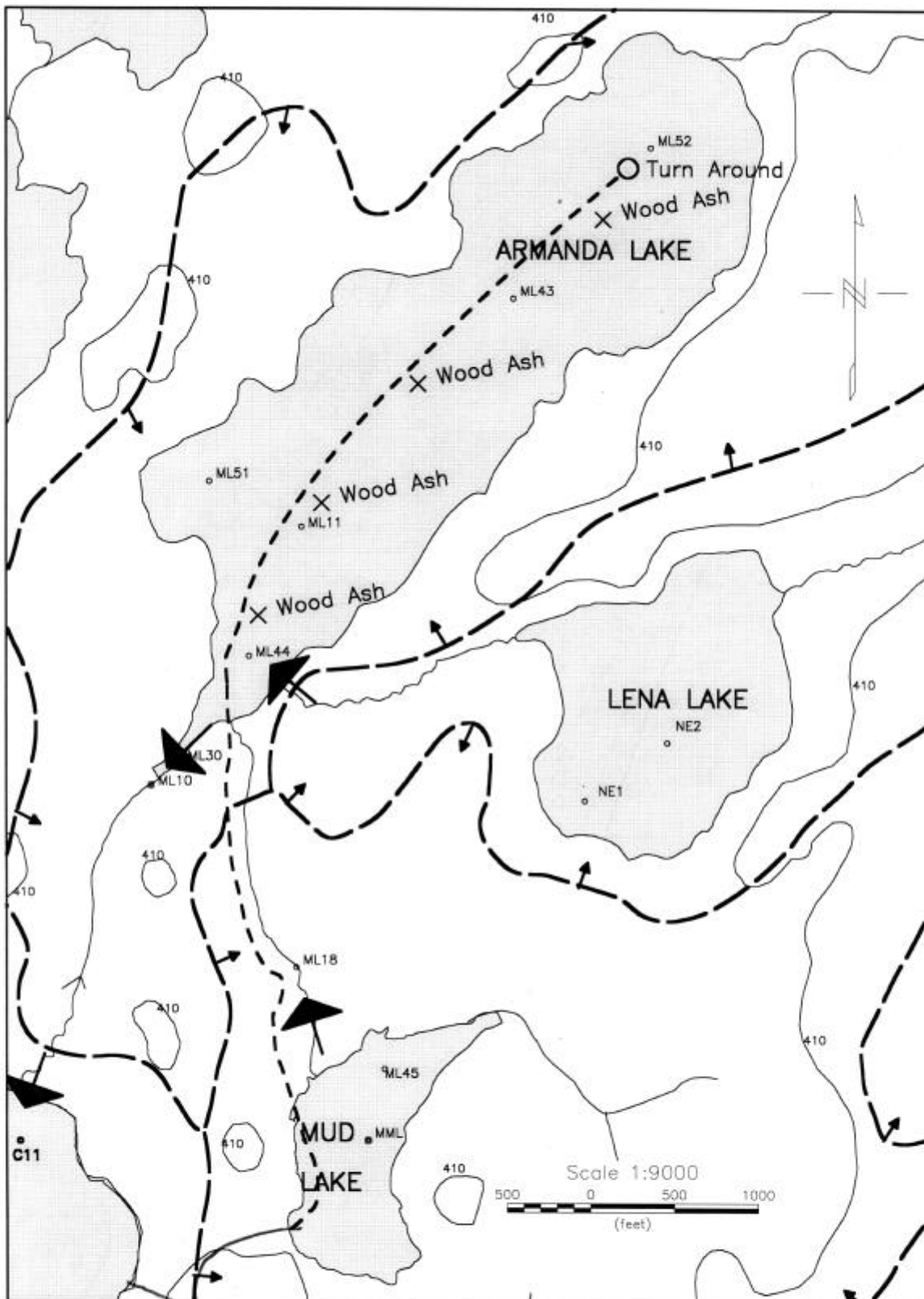
Fig. 15: Armanda L. - Treated ML18
Initial pH 5.41 : ML18 Input pH 2.7, then Apr 01, pH 10.78:
Beaver Dam Drained 06/00







Map 2: Sampling Location and Depth



Map 3: Wood-ash Distribution Locations



Plate 1: Installation of Phosphate Rock Distribution (The 'Titanic')



Plate 2: ARUM Enclosure with Iron Loading

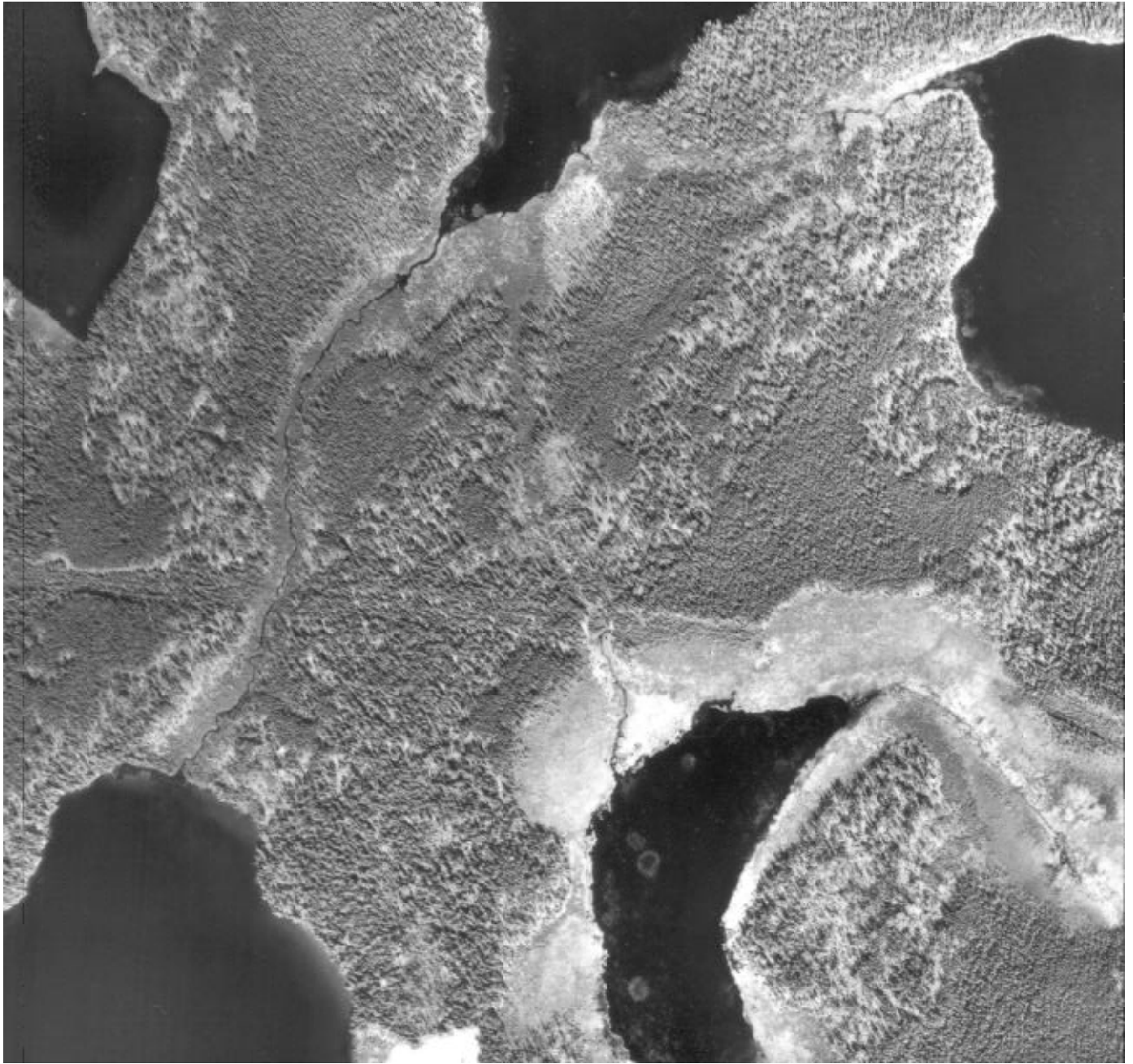


Plate 3: Area of Mud Lake Discharge